12

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CONTAINING

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AND

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN OTHER JOURNALS.

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,,	20, 23	$(NH_4)_2SO_4$	$\frac{1}{2}(NH_4)_2SO_4$.
,,	30	$(NH_4)_2SO_4 + KHO$	$\frac{1}{2}(NH_4)_2SO_4 + \frac{1}{2}K_2O$.
,,	31	K_2SO_4	$\frac{1}{2}K_2SO_4$.
,,	32	$(NH_4)_2SO_4 + NaHO$	$\frac{1}{2}(NH_4)_2SO_4 + \frac{1}{2}Na_2O$.
,,	33	Na_2SO_4	$\frac{1}{2}Na_2SO_4$.
,,	34	KHO	$\frac{1}{2}K_2O$.
,,	36	NaHO	$\frac{1}{2}Na_2O$

JOURNAL

OF

THE CHEMICAL SOCIETY.

I.—*Mineralogical Notices.*

By Professor N. STORY-MASKELYNE, Keeper, and Dr. WALTER FLIGHT, Assistant in the Mineral Department, British Museum.

1. ON THE FORMATION OF BASIC CUPRIC SULPHATES.

In 1867 M. Pisani described a mineral which he supposed to be the woodwardite of Mr. Church. The substance, however, is not the latter mineral. It had previously been examined in the laboratory of the British Museum, and the results sufficiently tallied with those of M. Pisani to enable us to identify the mineral.

It occurs in very thin crusts of various shades of yellow and green, the surface exhibiting a wavy appearance. Though the outer surface is occasionally somewhat compact, the mass is loose, and some of the layers pulverulent. Below are the results of the analyses of both portions:—

The inner layer—		
Copper oxide		24·561
Alumina		23·063
Calcium oxide		0·086
Magnesium oxide		0·749
Sulphuric acid		6·775
Silicic acid		6·689
Water—		
lost at ord. temperatures	15·39	
„ 100°	10·413	
„ 120°—260°	7·333	
„ over 260°	5·392	
		38·528
		100·451

The crust—

Copper oxide		10·255
Alumina		27·25
Calcium oxide		1·403
Magnesium oxide		6·183
Sodium oxide		0·643
Sulphuric acid		2·438
Silicic acid		7·53
Carbonic acid		0·528
Water—		
lost at ord. temperatures	13·938	
„ 100°—260°	23·864	
„ over 260°	6·167	
		43·969
		100·199

These numbers give us but little insight into the constitution of the mixed minerals. M. Pisani was right in regarding them as made up of langite and one or more hydrated aluminous silicates. The only interest they offer is in the light they seem to throw on the possible modes of the formation of native basic cupric sulphates.

The actions of solutions of magnesium- or calcium-sulphate on malachite in presence of carbonic acid may terminate in the production of langite, the alkaline earth being removed as acid carbonate, and the aluminous silicate may be looked on as an accidental ingredient, if not as a mechanical vehicle in which the langite has been retained.

An experiment in the laboratory showed that an insoluble cupric sulphate and acid magnesium carbonate were actually formed. Such experiments, however, obviously need much time for the process to be sufficiently complete to justify our assigning this as the *modus operandi* by which the minerals of the brochantite group have been formed in the mine.

2. Opal, Waddela Plain, Abyssinia.

Mr. Markham, geographer to the Abyssinian Expedition, presented to the British Museum some remarkable specimens of green opal from the above locality. The mineral is banded,

of a dark smoky green with occasional layers of white opal, resembling the prase opal of Faroe, its ribboned character recalling the structure of the onyx agate of that locality. Its exterior is weathered, and passes into a yellowish-white cacholong.

Most, but not all, of the water passed off at 100°, and the analysis of the mineral yielded the following numbers:—

Silicic acid (soluble)	90·562
Silicic acid (insoluble)	2·049
Water	5·656
Iron peroxide	0·933
Manganese oxide	Trace
Calcium oxide	0·137
Magnesium oxide	0·311
	99·648

3. Francolite, Cornwall.

To the localities of this mineral hitherto recorded, Wheal Franco, near Tavistock, and Fowey Consols, Mr. Talling added two years since a third as yet unnamed source. The matrix as before, is quartz and chlorite, but the new specimen is not associated, like that from Fowey Consols, with chalybite, whilst small quantities of pyrites accompany it. But the interest of the mineral lies in the fact that it contains a definite proportion of calcium carbonate; it is in fact a fluor-apatite in which one equivalent in every six of the calcium phosphate is replaced by carbonate. Analyses of several specimens gave the following results:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Calcium oxide	54·008	—	—	—	54·168	—	—	—
Iron and manganese oxide	0·937	—	—	—	0·786	—	1·016	—
Sodium oxide	—	—	—	—	0·694	—	—	—
Phosphoric acid	—	37·943	—	—	38·336	—	—	—
Carbonic acid	—	—	2·414	2·079	—	—	—	—
Fluorine	—	—	—	—	—	—	—	3·342
Water	—	—	—	—	—	1·593	—	—

The mean of these analytical results gives the subjoined numbers as indicative of the constitution of this mineral:—

		Equivalent ratios.
Tri-calcium phosphate.....	83·261	0·537
Calcium fluoride	7·683	0·197
Calcium carbonate	5·104	0·102
Iron and manganese oxide..	0·913	—
Sodium oxide	0·694	—
Water.....	1·593	—
	99·248	

The ratios point to the following formula:—

$$\left.\begin{matrix}5[Ca_3(PO_4)_2]\\ CaCO_3\end{matrix}\right\} + 2CaF_2.$$

That the calcium carbonate is present as an essential constituent is shown by the fact of the mineral dissolving in acid, with an effervescence which continues as long as any portion of the substance remains visible.

It is not a little remarkable that the francolite of Wheal Franco analysed by Mr. Henry* fell short of the full percentage by precisely the amount corresponding to the CO_2 found in the above analysis. In fact, the Wheal Franco francolite, as well as that of Fowey Consols, contains this ingredient.

This mineral contains no chlorine; its solution in hydrogen nitrate, when evaporated to dryness, strikes a fine violet tint, owing to the presence of a small amount of manganese.

The crystallography of this mineral seems also to point to its not being ordinary apatite, and, indeed, to its not being the same mineral as that from Wheal Franco, originally named francolite. This variety and that from Fowey Consols, while being so far similar in their chemical composition, that both contain calcium carbonate, are also similar in the composite nature of their crystals.

The true francolite consists of small well-defined hexagonal prisms, usually terminated by the basal plane 111. The crystals of the variety under description consist of little aggregated crystals, in which the prisms intersect with each other in a confused manner, which may arise from their being twinned; but with such minute and rough or tesselated surfaces it is impossible to determine the twin plane. The prisms are terminated by a low pyramid, the faces of which form, with those of the prism $2\bar{1}\bar{1}$, an angle which an average of several measure-

* Phil. Mag., 1850 [3], xxxvi, 134.

ments by the goniometer, with its object-glass used microscopically, gave as 72° 47′.

The summit plane 111 seems singularly enough to be always absent, a not common feature in a true apatite.

If we assume the angle 55° 40′, which Miller takes for that of the planes 111,100 of apatite, the plane in question may have for its symbol 744; the angle $2\bar{1}\bar{1}$,744 being by calculation 73° 41′, by observation 72° 47′.

It would be futile to modify the angle of the fundamental rhombohedron so as to bring this angle into more precise accordance with the measurements.

It is well known that the elementary angle varies in the apatites of different localities and composition; and it is quite probable that in this case also it is not quite the same as in ordinary fluor-apatite, but the measurements are not sufficiently exact to justify a modification of the elementary angle to meet them.

It is, however, clear from the above observations on the mineral from Fowey Consols and from the new locality, that it is not the same variety of apatite with that from Wheal Franco, nor indeed from any other locality.

4. Epidote and Serpentine, Iona.

Several green minerals occur in Iona, some of which have been miscalled Jade. One of these sent to the British Museum by the Duke of Argyll is a pebble in which the green mineral traverses bright red felspar and quartz in veins. Its specific gravity is 3·14 and hardness 6·5; it has a dull lustre and fracture and gives no indications of cleavage; its physical characters did not accord with those of epidote, nephrite, or serpentine. Its analysis gave the following numbers:—

		Oxygen ratios.
Silicic acid	51·565	27·50
Iron peroxide	13·519	4·05
Aluminium oxide	13·402	6·24
Calcium oxide	17·642	5·04
Magnesium oxide	0·642	0·25
Sodium oxide	1·400	—
Water	0·661	—
	98·831	

The percentages and oxygen ratios indicate a mixture of a lime-epidote with some 23 per cent. of quartz, the former mineral having the following constitution:—

$$3[2CaO,SiO_2] + 2[2(Al_{\frac{3}{5}}Fe_{\frac{2}{5}})_2O_3,3SiO_2].$$

This formula requires 17·77 per cent. Al_2O_3, and 18·65 per cent. Fe_2O_3 against 17·87 per cent. of the former and 18·03 per cent. of the latter oxide in the above analysis.

Greg and Lettsom mention Iona as a locality of epidote in association with clinkstone, and Jameson observes that epidote occurs at Icolmkill (*i.e.*, Iona) and Rona, in small veins with red felspar and quartz.

The other green stones from Iona were varieties of serpentine, some mixed with dolomite, others nearly pure and very translucent. The tint varies from greenish yellow to olive green, and a specimen of each extreme of colour was analysed. The yellow variety has a specific gravity of 2·52, a hardness nearly 4, and is given below as A. The green variety has a specific gravity of 2·574, a hardness of 3·5 to 4, and is B of the subjoined table:—

	A.	B.
Silicic acid	41·792	41·103
Iron protoxide	2·537	5·734
Calcium oxide	1·864	5·734
Magnesium oxide	39·262	32·882
Water	14·012	14·481
	99·467	99·934

These numbers accord tolerably well with the formula

$$3R''O,2SiO_2,2H_2O,$$

where R represents, in the first case, Mg with a little Fe and Ca; in the second Mg, nearly one-fifth of the equivalent of which is replaced by a mixture of equal equivalents of iron and calcium.

5. Vivianite.

For some time past specimens of vivianite, found by Mr. Talling in a new unnamed Cornish locality, have been in the hands of mineralogists. Some are beautifully crystallised, and present a very pale bluish-green tint; others are nodular in

form, deep blue in colour, and pulverulent in character, sometimes enclosing crystals or crystalline masses of incomplete form, dark brown colour, and exhibiting a reddish tint by reflected light.

The first of these varieties occurs generally in cavities with crystals of quartz and chalybite on a gangue, principally composed of blende, with a little galena, iron pyrites, copper pyrites, and some mispickel. It also occurs associated with hisingerite and limonite in cavities in massive iron pyrites, or again occasionally with bright and excellent crystals of scorodite, or with chalybite and cronstedtite on quartz. This assemblage of minerals much resembles that met with in some of the specimens from Old Wheal Kind, near St. Agnes.

The pale tinted and well crystallised variety has been examined crystallographically by Professor vom Rath.* When pounded in a mortar it rapidly changes from an almost colourless to a fine blue powder, evidencing an instability in the nature of the compound, which render precautions necessary in its analysis. When these precautions were taken, the mineral proved to be a nearly pure octahydrated ferrous orthophosphate. The following numbers were obtained in the analysis:—

	I.	II.	III.	Mean.	[$3FeO,P_2O_5,8H_2O$.]
Iron protoxide	42·358	43·06	—	42·709	43·028
Iron peroxide.....	—	—	1·126	1·126	—
Phosphoric acid	—	28·526	—	28·526	28·286
Water.....	—	28·984	—	28·984	28·686
				101·345	100·000

The brown crystalline variety contained in the nodules of pulverulent vivianite, when analysed, proved also to be almost pure orthophosphate, and no doubt the differences in colour that distinguishes the two minerals, must be due to difference in the degree of oxidation of a minute portion of the iron. The analysis of three separate specimens gave the following results:—

		[$3FeO,P_2O_5,8H_2O$.]
Iron protoxide	42·889	43·028
Iron peroxide	0·801	—
Phosphoric acid	28·792	28·286
Water	29·433	28·686
	101·915	100·000

* Pogg. Ann., cxxxvi, 405.

The earthy and friable mass which formed the bulk of the nodules enclosing the brown variety, was of a dark indigo-blue colour, and on analysis presented a much less simple composition than either of the previously described varieties. The following are the results of the analysis of this substance:—

	I.	II.	III.	IV.	V.	Mean.
Iron protoxide	—	36·928	—	37·501	—	37·214
Iron peroxide	—	—	—	—	—	9·169
Phosphoric acid	—	—	—	—	23·897	23·897
Carbonic acid	—	—	5·162	—	—	5·162
Water	23·825	—	—	—	23·918	23·871
Silica	—	—	0·811	—	—	0·811
Organic matter	—	—	0·826	—	—	0·826
						100·950

These numbers may be interpreted as representing five equivalents of octahydrated ferrous orthophosphate with one equivalent of octahydrated diferric phosphate mixed with four equivalents of ferrous carbonate. It would seem to have been the result of the decomposition, probably under the action of alkaline carbonated water, of the ferrous orthophosphate found in its purer form in the crystalline nucleus which is met with in almost every nodule.

The mineral collection at the British Museum contains some fine crystals of vivianite from Fernando Po, presented by Sir John Barrow, Bart., Secretary to the Admiralty. They are of very dark bluish black when viewed by reflected light, while light transmitted through portions of the crystal, acquires a fine indigo colour. Thin laminæ are often nearly colourless. The chemical examination of the vivianite from this locality gave the following result:—

	I.	II.	III.	IV.	
Iron protoxide	38·437	38·565	—	[43·076]	38·501
Iron peroxide	—	—	—	—	5·083
Phosphoric acid	—	—	—	27·802	27·802
Water	—	—	28·326	—	28·326
					99·712

Under IV the total iron is given as protoxide. It will be seen that this specimen stands intermediate between the blue and brown crystalline varieties on the one hand, and the blue

earthy mineral on the other. The oxygen-ratios of the above percentages correspond to a mixture of ten equivalents of octahydrated ferrous orthophosphate with one of the octahydrated diferric phosphate already spoken of as possibly present in the blue earthy variety of vivianite.

6. Cronstedtite.

Among the minerals already alluded to as associated with vivianite, is one of singular interest, as being known only in Pzribram and in Cornwall, and in both localities in great rarity. That mineral is cronstedtite. The specimens recently found in Cornwall by Mr. Talling present themselves in radiating groups on quartz, associated with blende, chalybite, iron pyrites, copper pyrites, a little galena, and mispickel, and occasionally fluor spar. The mineral also occurs in the form of a drusy coating on the killas. And it is met with in association with hisingerite* in acicular crystals in cavities on massive iron pyrites. The usual structure of this mineral is fibrous and radiating. The vitreous lustre of the marked cleavage-plane of the crystals which is parallel to their base, gives a sort of polyhedral surface to the fibrous masses.

The first analysis of this mineral gave the following numbers:—

		Theory.
Iron protoxide	36·307	41·54
Iron peroxide	36·762	30·77
Silicic acid.....	17·468	17·31
Water.....	10·087	10·38
Calcium oxide	0·087	—
	100·711	100·000

In juxtaposition with the analytical determinations are given the percentages required by the formula $3Fe''SiO_4 + 4\,(Fe_2)^{vi}H_6O_6$, which von Kobell assigned to this mineral. A considerable discrepancy exists between the numbers in the two columns as far as the oxides of iron are concerned, and may perhaps be due to an admixture of some iron hydrate, goethite for example, whose percentage of water corresponds with that of cronstedtite.

* Journ. Chem. Soc., viii, 5.

A second analysis with a fresh and more carefully selected material gave the following percentages:—

Iron protoxide	38·570
Iron peroxide	32·752
Silicic acid	18·546
Water	[10·132]
	100·000

The above numbers, though more nearly agreeing with, still differ somewhat from, those required by theory. Ascribing this disparity to an impurity in the specimen taken, a further quantity was picked over with the greatest care, and on analysis gave the number 41·272 as its percentage of iron protoxide, theory requiring 41·54 per cent.

It is possible that the excess of iron peroxide, silicic anhydride, and water in the first and second analyses over that required by cronstedtite, may result from a mixture with this mineral of some hydrated ferric silicate like hisingerite, with which in fact cronstedtite has been shown to be associated. The oxygen ratios of the excess of these constituents, however, will not allow us to assume them to be present in this form only. It is more than probable that during the weathering of the cronstedtite a portion of the silica may have been removed. If the silica in excess be left out of consideration, or supposed to be present only as an impurity, it will be found that the oxygen ratios of the excess of iron oxide and water correspond in each analysis with great precision to those of limonite.

The crystals of cronstedtite offer a problem of considerable interest to the crystallographer, from the hemimorphous character of the mineral. Hitherto, however, the only localities that have produced cronstedtite, namely, Pzribram and Wheal Maudlin—to which, perhaps, must be added the Brazilian locality Conghona, at which the mineral sideroschisolite, described by Wernekink, and probably identical with cronstedtite, has been found—failed to yield measurable crystals.

Among the specimens furnished by Mr. Talling, there were three or four on which the diverging groups of the crystals of cronstedtite presented here and there a crystal, or more generally a small group of crystals, with more definite crystalline features than usual. In some cases the crystals were mutually interpenetrating, the brilliant cleavage-planes of the different

crystals projecting through one another, presenting re-entering angles which indicated the probability of their being twinned. In most cases, again, a careful scrutiny of the bright summit plane showed it to be tesselated, and that the crystal was in fact composite, the different individuals comprising it being generally in parallel juxtaposition (Fig. 1), but sometimes (Fig. 2) twinned round the normal to that plane (the morpho-

Fig. 1. Fig. 2. Fig. 3.

logical axis of the crystal); but never so as to mask the truly hemimorphous character of the crystal.

The symmetry round the axis of each crystal is trigonal; the form of the crystal being that resulting from the combination of two rhombohedra, of which only the planes on one side of the unique plane of symmetry (that parallel to the summit plane) are extant. The crystal thus presents the aspect of a combination of two trigonal pyramids, of which one is more acute than the other. (See Fig. 3.)

Unfortunately the faces of these two forms are not only deeply striated, parallel to their vertical intersections, but are also invariably more or less rounded, the triangular summit plane of the crystal usually presenting in consequence a curved outline. With such unpromising planes, from which reflections are hopeless, it was very difficult to get trustworthy measurements. By operating on several crystals, however, and taking the average of the results, the following angles were obtained for the two rhombohedra:—

		Calculated.
111 on 100	= 85° 12′	85° 12′
111 on 522	= 75° 45′	75° 51′

Besides the twinning on the plane 111, it would seem also that the cronstedtite crystals are twinned on the plane 100. One angle observed on various crystals gave an average of—

		Calculated.
111 (100) $\bar{1}\bar{1}\bar{1}$	= 9° 42′	9° 36′

Another number found to recur in the measurement of the mutual inclinations of the planes 111 and $\bar{1}\bar{1}\bar{1}$ on different groups approximated to 19° 12′ (in four cases). Other recurrent numbers were very near 21° 30′ and 10° 15′.

In these cases the little crystals are very numerous, and interpenetrate each other in a very complicated manner. It was hoped by numerous measurements of the inclinations of the cleavage-planes on the different crystals (the only plane that was measurable), to deduce more trustworthy angles for the rhombohedron, on the plane of which it was assumed that the crystals in the group were twinned. In many cases, however, these measurements were rendered unreliable from the fact that the crystal cleaves so readily parallel to this single reflecting plane, that whenever pseudomorphous change has begun (to which cronstedtite seems peculiarly liable), or any mechanical cause, such as pressure, has disturbed the crystal, this plane has become distorted from its true position. And where only one plane on each crystal is amenable to geometrical measurement, it is almost hopeless to seek to determine the relative orientation of the axes of the different crystals forming a group.

This symmetry of the crystals suffices to prove that in cronstedtite we have an illustration of hemimorphism of a very interesting kind.

7. Pholerite.

This mineral was sent to the Museum from Capt. W. A. Ross, R.A., by the Secretary of State for India, and was called by Capt. Ross, meerschaluminite.

It is massive, of a pale flesh-white, has a dull, even fracture, and adheres to the tongue. Patches and veins of a black mineral penetrated the mass in several places.

An analysis of the flesh-white mineral gave the following results:—

Silicic acid		36·388
Aluminium oxide		34·594
Water:		
Combined	13·294	
Hygroscopic	15·019	
		28·313
		99·245

Traces of iron and manganese oxides accompany the aluminium oxide. Omitting the hygroscopic water, we have—

		Oxygen.
Silicic acid	43·144	23·009
Aluminium oxide.....	41·073	19·14
Water	15·783	14·029
	100·000	

This composition may be expressed by the formula, $2Al_2O_3$, $3SiO_2,4H_2O + SiO_2,H_2O$. Whether the silicic acid and water in excess of the formula for the silicate be uncombined with the alumina, or whether the minerals be a mixture of two hydrated aluminium silicates, such as pholerite with kaolinite, it was not thought necessary to investigate further. The mineral hardly needs a new name, the analysis according quite sufficiently with those of the pholerites; especially when it is considered that these uncrystallised products of the decomposition of other minerals are rarely so pure from admixture as to give a satisfactory formula. The black infiltrated substance exhibited the blowpipe reactions of manganese and cobalt, and contained, as did the pholerite, considerable traces of infiltrated nitrogenous organic matter.

By treating a portion of the mineral with an excess of solution of potassium hydrate, at 100° for several days, there were dissolved the following percentages of

		Oxygen.
Silicic acid	3·943	2·102
Aluminium oxide	7·482	3·487

II.—*On some Derivatives of Anthracene.*

By W. H. Perkin, F.R.S.

In the "Chemical News" of the 22nd July last, I published a short note upon some new derivatives of anthracene, and referred more particularly to the products resulting from the action of sulphuric acid upon dichlor- and dibromanthracene. I now beg leave to lay before the Society a more detailed account of my experiments in this direction, with the addition of a few other observations relating to the history of anthracene.

DICHLORANTHRACENE.

I have found it convenient to prepare this substance by passing chlorine gas over benzole holding about one-fifth its weight of purified commercial anthracene in suspension, until the mixture becomes a crystalline pasty mass. The product is then thrown on a linen filter, drained, and well washed with cold benzole. It is then dried and further purified, first by distillation, and then by two or three crystallisations from benzole. Thus obtained it presents itself as golden-yellow coloured needles.

Analysis of this product gave the following numbers:—

I. ·3151 of substance gave
·3624 of AgCl.
II. ·6258 of substance gave
·7333 of AgCl.
III. ·3607 of substance gave
·8974 of CO_2 and
·1073 of H_2O.
IV. ·3143 of substance gave
·7833 of CO_2 and
·0957 of H_2O.

These numbers agree with the formula—

$$C_{14}H_8Cl_2.$$

as the following comparisons show:—

	Theory.		Experiment.			
			I.	II.	III.	IV.
C_{14}....	168	68·02	—	—	67·85	67·97
H_8....	8	3·24	—	—	3·30	3·38
Cl_2....	71	28·74	28·45	28·95	—	—
	247	100·00				

It will be observed that these results perfectly agree with those of Graebe and Liebermann.* Dichloranthracene, when gently heated, sublimes in beautiful needles, which may be obtained of considerable size. It is fluorescent in the solid state as well as when in solution.

* Ann. Chem. Pharm., Supp. vii, 259 (1870).

When a boiling solution of dichloranthracene in benzole is added to a similar solution of picric acid, the mixture assumes a dark orange-red colour, and on cooling becomes filled with small bright red needles. These consist of a compound of dichloranthracene and picric acid. A determination of the dichloranthracene in this body gave numbers closely approximating to those required by the formula—

$$C_{14}H_8Cl_2,C_6H_3(NO_2)_3O.$$

Dibromanthracene.

The product used in my experiments was prepared by Graebe's process*. It was however purified first by distillation and then by crystallisation from benzole. Thus obtained it is of a golden-yellow colour. It gave on analysis the following numbers :—

·3205 of substance gave
·5864 of CO_2, and
·0729 of H_2O.

These numbers closely agree with those required by the formula—

$$C_{14}H_8Br_2,$$

as the following comparisons will show :—

	Theory.		Experiment.
C_{14}	168	50·00	49·9
H_8	8	2·38	2·52
Br_2	160	47·62	—
	336	100·00	

Like dichloranthracene, this body produces a beautiful red compound with picric acid.

Action of Sulphuric Acid on Dichloranthracene.

Dichloranthracene when submitted to the action of fuming sulphuric acid dissolves, forming a bright green solution, and is at the same time converted into a sulpho-acid.

To prepare this acid, one part of dichloranthracene is added

* Ann. Ch. Pharm. Suppl. vii (1870).

to about five parts of fuming sulphuric acid, and the mixture heated for a short time on the water-bath. It is then gradually poured into several times its bulk of water and treated with baric carbonate until all the sulphuric acid is neutralized. The acid solution when filtered off from the baric sulphate is evaporated to a small bulk. When sufficiently concentrated, it becomes on cooling a slimy mass of minute orange-yellow coloured crystals which may be drained on a porous tile.

This acid has not been analysed, but from the composition of its salts evidently possesses the formula—

$$C_{14}H_6Cl_2\left\{\begin{matrix}HSO_3\\HSO_3\end{matrix}\right..$$

I therefore propose to call it—*Disulphodichloranthracenic Acid.*—It is easily soluble in water, from which it is precipitated upon the addition of a little concentrated sulphuric or hydrochloric acid. It possesses a strongly acid taste and character. The dilute solutions of this acid and its salts are remarkably fluorescent, but not so strongly as an alkaline solution of pure Æsculine. The colour of the fluorescence is blue.

Sodic Disulphodichloranthracenate.—This salt can be obtained by neutralizing the acid with sodic carbonate, or from the calcic or crude baric salt by double decomposition. To obtain it from the latter, the product of the action of sulphuric acid on dichloranthracene is entirely neutralized with baric carbonate. Sodic sulphate is then added in the proportion of about five parts of dry salt to every ten parts of dichloranthracene employed, and the mixture well boiled; it is then filtered and the filtrate concentrated. On standing for some time, the new sodic salt separates in small orange-red crystals. These are well pressed between bibulous paper and purified by one or two crystallisations; dried at 150° C., they gave the following numbers on analysis:—

I.	·2284	grm.	of substance gave
	·0693	„	Na_2SO_4.
II.	·3449	„	of substance gave
	·4694	„	CO_2, and
	·0559	„	H_2O.

These numbers give percentages agreeing with those required by the formula—

$$C_{14}H_6Cl_2\left\{\begin{matrix}NaSO_3\\NaSO_3\end{matrix}\right.,$$

as the following comparisons will show:—

	Theory.		Experiment.	
			I.	II.
C_{14}	168	37·25	—	37·11
H_6	6	1·33	—	1·80
Cl_2	71	15·74	—	—
Na_2.....	46	10·20	9·83	—
S_2	64	14·19	—	—
O_6	96	21·29	—	—
	451	100·00		

This salt dissolves easily in water, forming an orange-coloured solution.

Baric Disulphodichloranthracenate.—This salt is best obtained in the pure state by the addition of baric chloride to a solution of the pure sodic salt. It is then thrown down as a bright canary-yellow coloured precipitate, nearly insoluble in water. The analysis of this salt gave the following numbers:—

I. ·2023 grm. of substance gave
·0859 „ $BaSO_4$.
II. ·0845 „ of substance gave
·0360 „ $BaSO_4$.
III. ·1534 „ of substance gave
·0658 „ $BaSO_4$.
IV. ·4179 „ of substance gave
·4637 „ CO_2, and
·0560 „ H_2O.
V. ·4117 „ of substance gave
·4549 „ CO_2, and
·0571 „ H_2O.
VI. ·3059 „ of substance gave
·3438 „ CO_2, and
·0448 „ H_2O.
VII. ·5936 „ of substance gave
·6767 „ CO_2, and
·0878 „ H_2O.

These give percentages agreeing tolerably well with the formula—

$$C_{14}H_6Cl_2Ba'' \left\{ \begin{matrix} SO_3 \\ SO_3 \end{matrix} \right.$$

The following is a comparison of the theoretical and experimental numbers:—

	Theory.		Experiment.						
			I.	II.	III.	IV.	V.	VI.	VII.
C_{14}....	168	30·99	—	—	—	30·26	30·13	30·65	31·09
H_6....	6	1·11	—	—	—	1·48	1·54	1·62	1·64
Ba....	137	25·28	24·96	25·05	25·22	—	—	—	—
Cl_2....	71	13·10	—	—	—	—	—	—	—
S_2....	64	11·81	—	—	—	—	—	—	—
O_6....	96	17·71	—	—	—	—	—	—	—
	542	100·00							

If to a hot solution of sodic disulphodichloranthracenate, strongly acidified with hydrochloric acid, baric chloride be added, no change at first is observed, but on standing a short time the above baric salt separates as an orange-coloured crystalline precipitate.

The following numbers were obtained on analyzing a specimen prepared in this manner:—

·1723 of substance gave
·0742 of $BaSO_4$ = 25·32 per cent. of barium.

Strontic Disulphodichloranthracenate.—On adding a solution of strontic chloride to a solution of sodic disulphodichloranthracenate, no apparent change takes place; but if the solution be evaporated, the new strontic salt separates in yellow crusts, difficultly soluble in water. A specimen gave the following numbers on analysis:—

·3146 of substance gave
·1136 of $SrSO_4$ = 17·21 per cent. of strontium.

The formula

$$C_{14}H_6Cl_2Sr'' \left\{ \begin{matrix} SO_3 \\ SO_3 \end{matrix} \right. \text{ requires } 17{\cdot}77 \text{ per cent.}$$

Calcic Disulphodichloranthracenate.—This salt may be obtained by neutralizing the product of the action of sulphuric acid on dichloranthracene with calcic carbonate, filtering

off the calcic sulphate, and evaporating the filtrate to dryness. The residue is extracted with water, filtered, and again evaporated. This salt is of a yellow colour, and easily soluble in water. It is useful for the preparation of the sodic salt by double decomposition with calcic carbonate.

Action of Sulphuric Acid upon Dibromanthracene.

Dibromanthracene dissolves in fuming sulphuric acid, forming a sulpho-acid. This has not, however, been prepared in a pure state, but from the examination of its salts it evidently possesses the formula—

$$C_{14}H_6Br_2\left\{\begin{matrix}HSO_3\\HSO_3\end{matrix}\right.,$$

and may therefore be called *disulphodibromanthracenic acid.* It is crystalline, and its dilute solutions are fluorescent, as also are its salts, but not nearly to the same extent as those of the corresponding dichloro-acid.

Sodic Disulphodibromanthracenate.—To obtain this salt one part of dibromanthracene is dissolved in the cold in about six or seven parts of fuming sulphuric acid, and the mixture allowed to stand for an hour or two. It is then gradually added to several times its bulk of cold water, well stirred, and neutralized with baric carbonate. Sodic sulphate is then added in the proportion of about five parts of dry salt to every twelve parts of dibromanthracene employed, and after boiling, the resulting sodic salt is filtered off from the baric sulphate, concentrated by evaporation over the water-bath, and set aside to crystallise. It is then well drained and pressed from the mother-liquor, and purified by two or three crystallisations from water.

Thus obtained, it is of a yellow colour, and crystallises in microscopic needles. It is easily soluble in water. It gave on analysis the following numbers:—

I. ·4676 of substance gave—
·1256 of Na_2SO_4 = 8·70 p.c. sodium.
II. ·4809 of substance gave—
·1311 of Na_2SO_4 = 8·85 p.c. sodium.

The formula

$$C_{14}H_6Br_2\left\{\begin{matrix}NaSO_3\\NaSO_3\end{matrix}\right. \text{ requires } 8{\cdot}52 \text{ per cent. of sodium.}$$

Baric Disulphodibromanthracenate.—This salt may be obtained in precisely the same manner as the corresponding disulphodichloranthracenate. It is obtained as a pale yellow precipitate. It gave on analysis the following result :—

·5565 of substance gave—
·2026 of $BaSO_4$ = 21·41 p.c. barium.

The formula

$$C_{14}H_6Br_2Ba''\left\{\begin{matrix}SO_3\\SO_3\end{matrix}\right. \text{ requires } 21{\cdot}71 \text{ per cent. of barium.}$$

This salt is remarkable for its insolubility. If a boiling solution of the sodic salt be strongly acidified with hydrochloric acid, and baric chloride added, the mixture, which is for a few seconds perfectly clear, becomes rapidly turbid with the formation of this salt, which cannot be re-dissolved, even by vigorous boiling, notwithstanding the excess of hydrochloric acid present.

Oxidation of Disulphodichloro- and Disulphodibromanthracenic Acid.—These sulpho-acids, when subjected to the influence of oxidizing agents, rapidly decompose, exchanging their chlorine or bromine for oxygen, and are thus converted into disulphanthraquinonic acid.

$$\underset{\text{Disulphodichloranthracenic acid.}}{C_{14}H_6Cl_2\left\{\begin{matrix}HSO_3\\HSO_3\end{matrix}\right.} + O_2 = \underset{\text{Disulphanthraquinonic acid.}}{C_{14}H_6(O_2)''\left\{\begin{matrix}HSO_3\\HSO_3\end{matrix}\right.} + ClCl$$

$$\underset{\text{Disulphodibromanthracenic acid.}}{C_{14}H_6Br_2\left\{\begin{matrix}HSO_3\\HSO_3\end{matrix}\right.} + O_2 = \underset{\text{Disulphanthraquinonic acid.}}{C_{14}H_6(O_2)''\left\{\begin{matrix}HSO_3\\HSO_3\end{matrix}\right.} + BrBr$$

An analogous result is also obtained by heating them with concentrated sulphuric acid, the following reactions taking place :—

$$C_{14}H_6Cl_2\left\{\begin{matrix}HSO_3\\HSO_3\end{matrix}\right. + H_2SO_4 = C_{14}H_6(O_2)''\left\{\begin{matrix}HSO_3\\HSO_3\end{matrix}\right. + 2HCl + SO_2$$

$$C_{14}H_6Br_2\left\{\begin{matrix}HSO_3\\HSO_3\end{matrix}\right. + 2H_2SO_4 = C_{14}H_6(O_2)''\left\{\begin{matrix}HSO_3\\HSO_3\end{matrix}\right. + BrBr + 2SO_2 + 2H_2O.$$

A quantity of disulphanthraquinonic acid, prepared by heating disulphodichloranthracenic acid with concentrated sulphuric acid, was made into the baric salt,* and analysed. The following results were obtained :—

I. ·2273 of substance gave—
·1040 of $BaSO_4$ = 26·90 p.c. barium.
II. ·3093 of substance gave—
·1415 of $BaSO_4$ = 26·89 p.c. barium.

The formula

$$C_{14}H_6O_2Ba''2SO_3 \text{ requires } 27{\cdot}23 \text{ p.c.}$$

Graebe and Liebermann have shown that dichlor- or dibrom-anthracene, when oxidized, also exchange their chlorine or bromine for oxygen, yielding anthraquinone.†

Whilst making the foregoing experiments, I have often been struck with the remarkable fluorescence of many of the anthracene products, anthracene itself, when pure and in large crystals, being one of the most beautifully fluorescent solid bodies I know of, though curiously its solutions are comparatively poor in this respect.‡ As this hydrocarbon, and also its chlorine derivative, which is fluorescent both in the solid state and in solu-

* I may here remark, that the baric disulphanthraquinonate although more soluble than the baric salts of the sulpho-acids obtained from dichlor or dibromanthracene is, like them, precipitated from hot solution in the presence of an excess of hydrochloric acid, if the solution be not too dilute; a specimen, prepared in this manner, gave the following results upon analysis :—

·2135 grm. of substance gave
·0981 $BaSO_4$ = 27·01 per cent.; theory, 27·23.

† When endeavouring to obtain some highly chlorinated anthracene derivatives, some time since, I came across a rather unexpected instance of this kind.

A quantity of dichloranthracene was suspended in glacial acetic acid and chlorine passed through the mixture. On allowing this to stand, a large quantity of a white product was obtained, which, when crystallised from benzole, was analysed, and gave of carbon 80·65 per cent., and of hydrogen 4·14 per cent. It was, in fact, anthraquinone, which requires of carbon 80·77, and of hydrogen 3·85, and had been formed owing to the presence of a small quantity of water in the glacial acetic acid, thus :—

$$C_{14}H_8Cl_2 + 2H_2O + Cl_2 = C_{14}H_8O_2 + 4HCl.$$

‡ The anthracene used in these experiments was chemically pure, and gave the following numbers on analysis :—

	I.	II.	Theory.
Carbon	94·31	94·37	94·38
Hydrogen	5·68	5·78	5·62

tion are volatile, it appeared to me interesting to examine them in the state of vapour. So far as I have gone, however, my experiments seem to show that the vapour of anthracene or dichloranthracene is not fluorescent, and moreover, a ray of light sent through a length of about 4 inches of the vapour of either body still retained its power of rendering fluorescent solutions luminous.

On sealing up anthracene in a long vacuum tube with platinum poles, and allowing the discharge from an induction coil to pass through the tube, nothing particular is observed, except the beautiful fluorescence of the crystals of anthracene. On examination with the spectroscope, the light showed carbon and nitrogen lines, the latter arising from the presence of a little air in the tube. Upon heating the tube, however, somewhat strongly, so as to volatilise the hydrocarbon, the ordinary colour of the discharge changed to a magnificent deep azure blue, and what is remarkable is that this blue light, when examined with the spectroscope, is perfectly continuous, and consists of blue with a little green.

Dichloranthracene, when treated in a similar manner, gives an analogous result, but suffers a good deal of decomposition, anthracene changing but little. These curious results do not appear to be due to the fluorescent character of the substances employed, as naphthalene produces a similar effect, the blue light, though not so intense, being continuous. It must be observed, however, that this hydrocarbon undergoes considerable change, becoming brown and oily.

Anthraquinone, heated in a vacuum tube in the same way, gives a greenish blue light, showing faint carbon bands.

On exposing a solution of disulpho-dichloranthracenic acid to the light of one of the recent displays of the aurora borealis, it was very strongly illuminated, as might be expected: moonlight, on the other hand, had no perceptible effect either upon it, or an alkaline solution of æsculin.

III.—*Researches on Vanadium.* Part III.

By Henry E. Roscoe, B.A., Ph.D., F.R.S.

(Abstracted from the Philosophical Transactions, 1870, p. 317.)

I. Metallic Vanadium.

In the second part of my "Researches on Vanadium,"* I stated that metallic vanadium absorbs hydrogen. This conclusion has been fully borne out by subsequent experiment; and it appears that the amount of absorbed or combined hydrogen taken up by the metal varies according to the state of division, first, of the chloride (VCl_2) from which the metal is prepared, and secondly, and especially, of the metallic powder itself. When the metal containing absorbed hydrogen is exposed to dry air, it slowly takes up oxygen, water being formed, and the vanadium undergoing oxidation to a substance which resembles the metal in its appearance, but possesses a darker grey colour, and has a less brilliant metallic lustre than vanadium itself. At this point the oxidation stops, although in most air it proceeds still further. Thus a portion of pure dichloride was reduced in hydrogen; of the reduced substance, free from chlorine, 0·2666 grm. yielded on complete oxidation 0·4441 of V_2O_5, corresponding to a percentage of 93·6 of pure metal. On exposure to the air for some days this substance absorbed oxygen, losing its brilliant metallic lustre; and when it was burnt in a current of dry oxygen, water was given off, thus:—

(1) 0·4232 grm. gave 0·0502 grm. of water and 0·6615 grm. V_2O_5,
(2) 0·2695 „ „ 0·0315 „ „ 0·414 grm. V_2O_5,

or

(1) gives 87·8 p.c. vanadium; 1·3 p.c. hydrogen; 10·9 p.c. oxygen.
(2) gives 86·7 p.c. vanadium; 1·3 p.c. hydrogen; 12·0 p.c. oxygen.

* Phil. Trans., 1869, p. 691; Chem. Soc. J. [2], viii, 344.

The difficulty of obtaining metallic vanadium perfectly free from admixture of oxide was again rendered evident. Pure tetrachloride was prepared in quantity, and from this the dichloride was made. On heating this dichloride to whiteness for forty-eight hours, a substance was obtained, which gained on oxidation 70·7 per cent., and therefore still contained a slight admixture of oxide. The reducing action of sodium on the solid chlorides was next examined; in this case the reduction takes place rapidly but quietly in an atmosphere of hydrogen, at a red heat, and may be best conducted in strong iron tubes, proved air-tight under hydraulic pressure of 200 lbs. on the square inch. Explosions occur when the tetrachloride is heated with sodium. The substance thus obtained by the action of sodium was found on lixiviation to be free from chlorine, and on washing it was found to separate into two parts—(1) a light and finely divided black powder (trioxide), soluble in hydrochloric acid, which remains in suspension; and (2) a heavier grey powder (insoluble in hydrochloric acid), which is deposited, and which by repeated washing may be entirely freed from the lighter trioxide. This bright grey powder consists of metallic vanadium mixed with more or less oxide. If the finely divided metallic powder, after drying *in vacuo*, be reduced at a low red heat in a current of pure hydrogen, it takes fire spontaneously, when cold, on exposure to air or oxygen, a distinct flame being seen playing on the surface, whilst water is formed. In one experiment a product thus prepared contained 91·1 per cent. of metallic vanadium (0·354 substance gave 0·574 grm. V_2O_5). This substance, exposed for some weeks to dry air, slowly absorbed oxygen, and on roasting gave a percentage increase of 53·75 (0·453 grm. yielded 0·6965 V_2O_5), whilst 0·034 grm. or 7·5 per cent. of water was at the same time formed. This shows that the point of oxidation at which the metal containing hydrogen becomes stable in dry air corresponds nearly to the oxide V_2O.

A similar slow change in the appearance of the metal has been noticed in some portions of the metallic powder placed on microscopic slides.

II. Vanadium and Bromine.

1. *Vanadium Oxytribromide or Vanadyl Tribromide*, $VOBr_3$, molec. wt. = 307·3.—When the vapour of perfectly dry and

pure bromine is passed over vanadium trioxide (V_2O_3) heated to redness, dense yellowish-white fumes of the oxytribromide are formed in the heated portion of the tube, and these condense together with the excess of bromine to form a dark red transparent liquid. In order to free the oxytribromide from excess of bromine, the mixed liquids must be rectified *in vacuo*, as the temperature of decomposition of the oxybromide lies (under the ordinary atmospheric pressure) below its boiling-point. By distilling under a pressure of 106 millims. of mercury in a current of perfectly dry air, the whole of the bromine was got rid of before the thermometer rose to 45° C. The transparent liquid remaining in the retort had a dark red colour, gave off white fumes on exposure to moist air, and when thrown into water produced a light yellow solution of a vanadic salt. It is possible to distil the oxybromide under diminished pressure with but slight decomposition occurring, although when heated under the atmospheric pressure it suddenly solidifies at 180° C., splitting up into the oxydibromide and bromine. Under a pressure of 100 millims. of mercury the oxytribromide volatilizes without decomposition between 130° to 136° C.

The following analytical results were obtained:—Analysis No. 1 was made from a portion of oxytribromide which had not been distilled; No. 2 from a portion of the same substance, after further treatment with dry air at 63°; No. 3 from another preparation which had been distilled *in vacuo*, and in which the bromine determination is too high owing to traces of free bromine.

The composition of the oxytribromide is as follows:—

		Calculated.		Found.			Mean.
				I.	II.	III.	
V	=	51·3	16·69	16·52	16·87	16·62	16·67
Br_3	=	240·0	78·10	79·62	79·10	80·48	79·36
O	=	16·0	5·21	—	—	—	—
		307·3	100·00				

The colour of the oxytribromide is somewhat redder than that of bromine, and it is more transparent in thin films, and much more translucent than bromine.

The oxytribromide slowly decomposes at the ordinary atmospheric temperature into bromine and oxydibromide; it is very deliquescent and hygroscopic, and cannot be formed in presence

of moisture. The specific gravity of the oxytribromide at 0° is 2·9673, and at 14°·5 it is 2·9325.

2. *Vanadium Oxydibromide or Vanadyl Dibromide*, $VOBr_2$, molec. wt. = 227·3.—This substance forms suddenly when the oxytribromide is heated to temperatures above 180°, and it is slowly produced by the same decomposition at lower temperatures. The oxydibromide is a yellowish-brown solid body, in appearance resembling ochre; it is very deliquescent, and on heating in the air it loses all its bromine and is converted into the pentoxide. Thrown into water it dissolves, furnishing a blue solution of hypo-vanadic (V_2O_4) salt.

Its composition is as follows:—

	Calculated.		Found.		Mean.
V	51·3	22·57	23·40	21·50	22·45
Br_2....	160·0	70·39	71·75	70·11	70·93
O	16·0	7·04	—	—	—
	227·3	100·00			

3. *Vanadium Tribromide*, VBr_3, molec. wt. = 291·3.—This body condenses as a greyish black opaque amorphous sublimate, when dry bromine vapour is passed in excess over vanadium nitride heated to redness. Brown vapours are given off, which soon condense in the cooler portions of the tube. The tribromide is a very unstable compound, losing bromine, even at the ordinary temperature in dry air, and being converted into V_2O_3 when gently heated. It deliquesces rapidly on exposure to moist air, giving rise to a brown liquid, in this respect resembling the trichloride; but on addition of a few drops of hydrochloric acid the brown liquid changes to the green colour characteristic of a solution of vanadous salt (V_2O_3). No free bromine is evolved when the tribromide dissolves in water. In order to prepare the tribromide, pure nitride of vanadium, contained in a porcelain boat, was introduced into a combustion tube, and after all the air had been displaced by dry carbonic acid, the part of the tube containing the nitride was heated to redness, the other part of the tube being kept at such a temperature as to volatilize any excess of bromine which might pass over. After all the nitride had burnt away, the bulb containing the bromine was sealed off and a current of dry carbonic acid passed over the solid bromide

to displace all traces of free bromine. A second method of preparing the tribromide is to pass bromine vapour over a mixture of vanadium trioxide and charcoal; in this reaction the oxytribromide is first formed, then the oxydibromide, and lastly, the tribromide, VBr_3; but this plan is not to be recommended, as the tube soon becomes stopped up by the formation of these solid compounds. The bromide thus prepared was not analysed, but it presented exactly the same appearance and properties as the tribromide obtained by the first method.

No higher compound of bromine and vanadium than the tribromide could be obtained. The volatile liquid passing into the bulb in the first preparation was carefully rectified, and it was all found to distil over at the boiling point of bromine, leaving only a small quantity of the tribromide in the bulb. Some difficulty was experienced in obtaining satisfactory analytical results with the tribromide, owing to the fact, already observed by Stas,* that bromide of silver, when boiled with excess of nitrate of silver, carries down with it some of this latter salt inclosed in the bromide, and that this impurity cannot be got rid of by washing. Owing to this admixture of nitrate of silver, the bromine determinations usually come out about two per cent. too high, whilst the vanadium determinations gave constant numbers, agreeing much more nearly with the calculated results. Thus in four analyses of the tribromide prepared on different occasions the mean percentage of bromine was found to be 84·15, the calculated percentage being 82·4; whilst the vanadium determinations of the same portions gave 18·57 per cent. instead of 17·6 per cent. In order to lessen as much as possible this error, the precipitated bromide of silver was reduced in hydrogen until no further diminution of weight occurred, and the percentage of bromine calculated from this loss.

	Calculated.		Found.			Mean.
V =	51·3	17·6	18·46	18·80	18·52	18·59
Br_3 =	240·0	82·4	81·21	80·58	80·78	80·86
	291·3	100·0	98·67	99·38	99·30	99·45

Experiments made with the bromine employed, which had been rectified over potassium bromide, and was carefully tested

* Stas, Recherches sur les Lois des Proportions chimiques, p. 156.

for chlorine and iodine and shown to be pure, proved that a similar excess of weight occurred on precipitation with nitrate of silver. In one experiment the percentage of bromine thus found was 100·96, and in a second experiment 101·41. The bromine determinations of the oxybromides are similarly all too high from the same cause.

III. Vanadium and Iodine.

When vapour of iodine is passed over the red-hot nitride of vanadium contained in a tube, no action whatever takes place, the nitride after the operation remaining perfectly unchanged. Vanadium trioxide is likewise unacted upon by iodine at all temperatures.

IV. Metallic Vanadates.

In the first part of these researches* I pointed out (1) that the vanadates analysed by Berzelius, prepared by boiling vanadic acid with the alkaline hydroxides and by double decomposition, must be considered as meta- or monobasic vanadates, (2) that the so-called bi-vanadates analysed by Von Hauer,† and prepared by acting on the metavanadates with acids, are anhydro-salts, and (3) that the naturally occurring vanadates are tribasic salts, and that sodium ortho-vanadate is formed when one molecule of vanadium pentoxide is fused with three molecules of carbonate of soda, three molecules of carbon dioxide being expelled. I have now to describe the preparation and properties of some characteristic members of these three classes of vanadates, as well as those of a fourth new class, viz., the tetrabasic or pyro-vanadates.

Determination of Vanadium in the Soluble Vanadates.—The separation of vanadic acid from the metals of the alkalies by means of chloride of ammonium, as proposed by Von Hauer, is apt to give too low results, both as regards the vanadium and the alkali. It is almost impossible to prevent traces of ammonium metavanadate from dissolving, and on ignition, even with the greatest care, some portions of the finely-divided vanadium pentoxide are invariably carried off when the ammonia escapes.

* Philosophical Transactions, 1868 (Bakerian Lecture); Chem. Soc. J. [2], vi, 322.
† Journ. prac. Chem., Bd. lxix, p. 388, 1856.

On the other hand, the volatilization of the comparatively large quantities of sal-ammoniac which must be employed in order to ensure the complete precipitation of the vanadium, almost always entails a considerable loss of the fixed alkaline chlorides. A far more accurate plan for the separation of vanadium is the precipitation of the soluble vanadate by acetate of lead, when basic lead vanadate is precipitated, which is so insoluble that a portion when finely powdered and boiled in water did not dissolve in sufficient quantity to enable the lead to be detected in the filtrate with sulphuretted hydrogen. This salt is also insoluble in acetic, but dissolves readily in nitric acid, liberating vanadic acid, which separates out, but dissolves completely when the liquid is warmed. In the analysis of a soluble vanadate this insoluble lead salt is collected on a filter, dried at 100° C. and weighed; a given quantity of the dried salt is then dissolved in nitric acid, the lead precipitated by pure sulphuric acid, and the lead sulphate determined, with the usual precautions of evaporation with addition of alcohol, &c. The lead sulphate thus obtained is (contrary to Berzelius's statement) quite free from vanadium, whilst the vanadic acid in the filtrate is obtained perfectly pure, and well crystallised on evaporation and ignition. The filtrate from the lead vanadate, freed from excess of lead by means of sulphuric acid and evaporated, yields the alkaline sulphate not containing a trace of vanadium.

Sodium Vanadates.

1. *Sodium Orthovanadate*, $Na_3VO_4 + 16H_2O$.—When a mixture of three molecules of sodium carbonate and one molecule of vanadium pentoxide is fused until no further evolution of carbon dioxide is observed, three molecules of CO_2 have been expelled and a tribasic vanadate remains as a white crystalline mass.

In one experiment in which a slight excess of sodium carbonate was taken, 0·5785 grm. V_2O_5 liberated on fusion 0·4185 grm. CO_2. According to the equation—

$$V_2O_5 + 3Na_2CO_3 = 2Na_3VO_4 + 3CO_2,$$

the weight of CO_2 liberated by this quantity of vanadium pentoxide is 0·4182 grm.

The mixture is easily fusible at first, but becomes less so as

the reaction proceeds; whilst to begin with the heat of a Bunsen's burner is sufficient to melt the mass, it is necessary to apply the heat of a blowpipe-flame to keep up the fusion when the decomposition becomes more nearly complete. On cooling, the solidified mass acquires first a dark green colour, and then passes through yellow, until when cold it becomes perfectly white, and is found to possess a crystalline appearance. It dissolves easily in cold water, but is insoluble in alcohol. Hot water must *not* be employed for dissolving the fused mass, and as little cold water as possible. The cold, strong aqueous solution must be instantly mixed with excess of strong alcohol; two layers of liquid are then formed, the upper one consisting of dilute alcohol, the lower one of the saline solution. After standing for a few hours the lower layer of liquid solidifies, forming an aggregate of colourless needle-shaped crystals. These crystals, which possess a strong alkaline reaction, are washed with small quantities of alcohol, then placed on a porous plate over sulphuric acid *in vacuo*, and after remaining for a short time they may be taken out for analysis.

The analysis yielded the following results :—

	Calculated.		Found.
Na_3....	69·0	14·61	13·80 per cent.
V.....	51·3	10·86	10·86 „
O_4	64·0	13·56	—
$16H_2O$..	288·0	60·97	60·44 „
	472·3	100·00	

Sodium orthovanadate is an extremely unstable compound. Its aqueous solution slowly undergoes decomposition on standing at the ordinary temperature of the air out of contact with atmospheric carbonic acid, whilst at higher temperatures the same change takes place quickly. This decomposition consists in the formation of a new salt, sodium tetravanadate, the liquid becoming strongly alkaline, whilst caustic soda is liberated, according to the equation—

$$2(Na_3VO_4) + H_2O = Na_4V_2O_7 + 2NaHO.$$

This remarkable reaction was carefully investigated, as is seen in the sequel.

I have not been successful in several attempts to prepare a

tribasic sodium vanadate containing basic hydrogen. All the reactions which, with the corresponding phosphates yield hydrogen-sodium salts, give with the vanadate the tetrabasic compound above mentioned. The orthovanadates of most of the metals are insoluble compounds obtained by precipitating neutral solutions of the soluble metallic salts with a solution of orthovanadate of sodium. The reactions of the more important metals are as follows:—

Reaction of the Orthovanadates.

1. Ferric salt	Gelatinous precipitate of a light brownish-yellow colour, soluble in hydrochloric, insoluble in acetic acid.
2. Ferrous salt.....	Dark grey precipitate.
3. Manganous salt ..	Brownish-yellow crystalline precipitate.
4. Zinc salt	White gelatinous precipitate.
5. Cobalt salt	Brown-grey gelatinous precipitate.
6. Nickel salt	Canary-yellow crystalline precipitate.
7. Aluminium salt ..	Bright yellow gelatinous precipitate, soluble in excess of both reagents; on boiling a white precipitate is again thrown down.
8. Copper salt	Apple-green precipitate.
9. Mercuric salt	Orange-yellow precipitate.

The reaction which serves best to distinguish the ortho- from the metavanadates is that of the corresponding copper salts. Orthovanadate of copper possesses a bright apple-green colour, whilst the metavanadate falls down a light yellow crystalline powder.

2. *Tetrasodium Vanadate*, or *Pyrovanadate*, $Na_4V_2O_7 + 18H_2O$.—This salt crystallises in beautiful six-sided tables. It is easily soluble in water, insoluble in alcohol, and is precipitated from aqueous solutions by the latter liquid in the form of white scales of a pearly lustre. The pyrovanadate can be readily obtained by fusing one molecule of vanadium pentoxide (V_2O_5) with two molecules of sodium carbonate (Na_2CO_3) dissolving, and crystallising. It can also be obtained by the decomposition of the orthovanadate in aqueous solution. As long as the tetrabasic salt contains free alkali, from the decomposition of the ortho-

vanadate, the precipitate with alcohol forms oily drops, which solidify after some time only, whilst the pure salt is at once thrown down in the form of silky scales. If the fusion of vanadium pentoxide with three molecules of carbonate of soda be not completed at a very high temperature, the carbonate is not fully decomposed, and the fused mass when dissolved in water crystallises at once in six-sided tables, or, if the solution be very concentrated, in nodular groups of needle-shaped crystals. The tetrabasic salt is more easily fusible than the tribasic salt, and on cooling from fusion it also forms a crystalline mass.

	Calculated.		Found.					Mean.
Na_4	92·0	14·58	14·67	14·79	14·57	—	—	14·68
V_2.....	102·6	16·27	16·29	15·71	15·60	16·19	16·06	16·06
O_7.....	112·0	17·77	—	—	—	—	—	—
$18H_2O$..	324·0	51·38	50·69	53·40	51·44	—	—	51·84
	630·6	100·00						

When a solution of tetrasodium vanadate is treated with carbonic acid, the salt is decomposed into sodium carbonate, which crystallizes out, and sodium metavanadate, which being the more soluble salt, remains in solution; thus:—

$$Na_4V_2O_7 + CO_2 = 2NaVO_3 + Na_2CO_3.$$

The insoluble pyrovanadates precipitated in solutions of the various metals possess properties generally similar to those of the corresponding tribasic vanadates.

Calcium Vanadates.

If to a freshly prepared solution of trisodium vanadate a solution of chloride of calcium be added, a white precipitate falls down, whilst the liquid possesses a strongly alkaline reaction, and absorbs carbonic acid from the air. The precipitate is a mixture of calcium pyrovanadate and calcium hydroxide; the tribasic calcium salt, therefore, cannot thus be obtained, as it at once decomposes as follows:—

$$Ca_3V_2O_8 + H_2O = Ca_2V_2O_7 + CaH_2O_2.$$

Calcium Pyrovanadate, $Ca_2V_2O_7 + 2\frac{1}{2}H_2O$.—This compound is precipitated as a white amorphous powder when a solution of

chloride of calcium is added to one of the tetrabasic sodium salt. The salt dried at 100° C. exhibited the following composition:—

	Calculated.		Found.
Ca_2	80·0	23·56	23·23
V_2.....	102·6	30·21	30·16
O_7.....	112·0	32·98	—
$2\frac{1}{2}H_2O$.....	45·0	13·25	12·63
	339·6	100·00	

Barium Pyrovanadate, $Ba_2V_2O_7$.—The dibasic barium salt is anhydrous, but otherwise it closely resembles the corresponding calcium compound. It is slightly soluble in water. For analysis it was dried at 100° C.

	Calculated.		Found.
Ba_2	274·0	56·08	54·69
V_2.....	102·6	20·99	21·50
O_7.....	112·0	22·93	—
	488·6	100·00	

Lead Vanadates.

Three native lead vanadates are known.

(*a*) Lead metavanadate, $Pb(VO_3)_2$, occurs as Dechenite.

(*b*) Lead pyrovanadate, $Pb_2V_2O_7$, occurs as Descloizite.

(*c*) Lead orthovanadate and lead chloride, $3Pb_3(VO_4)_2 + PbCl_2$, occurs as vanadinite.

1. *Basic Pyrovanadate of Lead*, $2Pb_2V_2O_7 + PbO$.—When a solution of the tetra-sodium vanadate is mixed with a solution of lead acetate, a pale yellow precipitate is thrown down, and the liquid acquires an acid reaction.

The properties of this salt have already been described.

For analysis the salt was dissolved in nitric acid, and (with the exception of No. 1) the lead precipitated by sulphuric acid. The sulphate of lead was found to be quite free from vanadium, and the vanadic acid contained no lead, provided care had been taken to remove all nitric acid by evaporation, and if the liquid was mixed with alcohol before the lead sulphate was filtered.

	Calculated.		Found.				Mean.
Pb_5	1035·0	69·92	70·92	69·85	69·83	70·57	70·29
V_4	205·2	13·86	13·55	12·98	13·52	13·03	13·27
O_{15}	240·0	16·22	—	—	—	—	—
	1480·2	100·00					

2. *Lead Orthovanadate*, $Pb_3(VO_4)_2$.—The tribasic vanadate of lead falls as an insoluble nearly white powder when tribasic sodium salt is precipitated by lead acetate. 0·7245 of the substance, when decomposed by nitric acid and precipitated by sulphuric acid, yielded 0·1515 of V_2O_5, or contained 11·75 per cent. of vanadium, the percentage required by the formula being 12·04.

3. *Lead Orthovanadate and Lead Chloride; artificial Vanadinite*, $3(Pb_3(VO_4)_2)PbCl_2$, or lead trivanado-chlorhydin, $\left.\begin{matrix}3VO''' \\ Pb_5\end{matrix}\right\}\begin{matrix}O_9 \\ Cl\end{matrix}$.

If oxide of lead, vanadic acid, and chloride of lead be fused together for a few hours in the proportions in which they are contained in the above formula, the mass after slowly cooling is found to consist of a greyish-yellow crystalline substance, in the interstices of which groups of needle-shaped crystals occur. The fused mass on boiling in water is soon reduced to a powder entirely consisting of fine crystals. This crystalline powder is boiled with water until no further trace of chlorine can be detected in the washings when it is dried ready for analysis. The crystals obtained were too small for measurement; they were, however, seen to consist of hexagonal prisms; the faces of the hexagonal pyramid could not be identified. The crystals have a yellow colour, and possess the waxy lustre characteristic of the natural mineral.

The following gives the composition of various specimens of natural vanadinites compared with that of the artificial mineral:—

	Calculated. $3(Pb_3(VO_4)_2)PbCl_2$.	Natural vanadinites. Zimapan (Berzelius).	Windischkappel (Rammelsberg).	Wieklow.	Beresesowsk (Struve).	Artificial vanadinites. (1)	(2)
Lead	73·08	70·40	71·20	68·72	73·76	71·96	71·57
Vanadium .	10·86	—	9·77	13·15	9·54	11·11	—
Phosphorus.	—	—	—	—	1·34	—	—
Chlorine ..	2·56	2·54	2·23	2·44	2·46	2·33	2·17
Oxygen	13·55	—	—	—	—	—	—

The specific gravity of the artificial vanadinite at 12° C. is 6·707, that of the natural mineral varies from 6·66 to 7·2*.

Silver Vanadates.

1. *Silver Orthovanadate, or Tribasic Silver Vanadate*, Ag_3VO_4, is precipitated as a deep orange-coloured powder when a freshly prepared solution of tribasic sodium salt is mixed with a perfectly neutral solution of silver nitrate. If the precaution of neutralizing the silver solution with carbonate of soda, filtering, and boiling be not adopted, a salt is precipitated which consists of a mixture of tribasic and tetrabasic silver salt. The colour of this mixed salt is lighter than that of the tribasic compound, and it gives on analysis a percentage of silver and vanadium intermediate between the two salts.

Silver orthovanadate is easily soluble in nitric acid and ammonia. For analysis it was dissolved in nitric acid, the silver being precipitated as chloride, and the vanadium estimated in the filtrate.

	Calculated.		Found.		Mean.
Ag_3 ..	324·0	73·75	74·12	73·54	73·83
V	51·3	11·67	11·59	11·94	11·86
O_4....	64·0	14·58	—	—	—
	439·3	100·00			

2. *Tetrabasic Silver Vanadate*, $Ag_4V_2O_7$.—This salt is prepared by precipitating a solution of pure tetrasodium salt with a neutral solution of silver nitrate. It is a dense yellow precipitate, settling very easily when the liquid is warmed, and resembling in its appearance ordinary tribasic phosphate of silver.

	Calculated.		Found.
Ag_4	432·0	66·81	66·45
V_2.....	102·6	15·87	15·99
O_7.....	112·0	17·32	—
	646·6	100·00	

* Pyromorphite and apatite were prepared artificially for the first time in 1852 by Manross (Ann. Ch. Pharm. lxxxii, p. 348), and afterwards by Deville and Caron, and Debray. Mimetesite has also been recently artificially prepared by Lechartier (Comptes Rendus, 1867, lxv, p. 172).

From the foregoing experiments on the vanadates it appears:

(1) That the soluble tribasic salts are less stable at the ordinary temperature than the tetrabasic compound, Na_3VO_4, splitting up in solution into free caustic soda and the pyro-salt.

(2) That at a high temperature, on the other hand, the tribasic form is the most stable, V_2O_5 liberating three molecules of CO_2 when fused with carbonate of soda, but forming a monobasic (meta) salt when boiled with a solution of alkaline carbonate.

(3) That as the majority of the naturally occurring vanadates are tribasic compounds, we may assume that these have been produced at a high temperature.

(4) That in aqueous solutions the soluble pyrovanadates are easily decomposed by carbonic acid into an alkaline carbonate and a monobasic or metavanadate.

Hence the order of stability of the different vanadates at the ordinary temperatures is as follows:—

(1) Monobasic or metavanadates.
(2) Tetrabasic or pyrovanadates.
(3) Tribasic or orthovanadates.

In the phosphorus series the order of stability is (as is well known) exactly the reverse of this, the tribasic phosphoric acid and soluble orthophosphates being most stable, and being formed from the other two classes of acids and soluble salts, either by ebullition alone or in presence of weak acids.

IV.—*On some New Derivatives of Coumarin.*

By W. H. Perkin, F.R.S.

In May last I had the honour of laying before the Society a short account of some derivatives of this interesting product. Since that time I have procured further information upon the substances I then described, and have also obtained a number of new derivatives of coumarin. I now beg leave to bring an account of my results before the Society.

Dibromide of Coumarin.

When preparing this product I originally mixed a solution of coumarin in disulphide of carbon with a similar solution of bromine, using these substances in theoretical proportions. The resulting solution was then allowed to evaporate spontaneously, and the product purified. By this method I obtained a very poor yield of the dibromide. I have since found that if the solution of bromine and coumarin be kept for twelve hours or more previous to the evaporation of the disulphide, a much larger yield of product is obtained, 5 grms. of coumarin generally yielding from $7\frac{1}{2}$ to 8 grms. of dibromide.

Dibromide of coumarin, when mixed with an alcoholic solution of potassic iodide, becomes brown, and on evaporation deposits metallic-looking needles, apparently consisting of a mixture of iodine and coumarin crystallised together.

α. Bromocoumarin.

Upon referring to the previous method given for the preparation of this body, it will be found that it was obtained from the mother-liquors of dibromocoumarin. If, however, a mixture of bromine and coumarin (mixed with disulphide of carbon) in the proportion of two parts of the former to one of the latter, be heated in a sealed tube to about 200° C. for three or four hours, the resulting product will consist almost entirely of monobromocoumarin.

In this reaction dibromocoumarin is undoubtedly first produced, but at the high temperature employed it is decomposed

by the hydrobromic acid produced, losing half of its bromine, thus—

$$\underset{\text{Dibromocoumarin.}}{C_9H_4Br_2O_2} + HBr = \underset{\text{Bromocoumarin.}}{C_9H_5BrO_2} + BrBr.$$

The bromocoumarin obtained by this process sometimes crystallises from alcohol in long slender needles; these, however, on standing in the mother-liquor for a few days become short and hard, like those described in my previous paper; in fact, so different was the appearance of this body when freshly crystallised from that which I had previously obtained, that I subjected it to analysis. The following are the results obtained:—

I. ·4440 of substance gave
·3710 of AgBr.
II. ·3436 of substance gave
·5986 of CO_2, and
·0702 of H_2O.

	Theory.		Experiment.	
			I.	II.
C_9	108	48·00	—	47·51
H_5	5	2·22	—	2·27
Br	80	35·56	35·56	—
O_2	32	14·22	—	—
	225	100·00		

I have, however, found a still more simple process for the preparation of bromocoumarin than the above. It consists in the decomposition of the dibromide of coumarin with alkalies, the following reaction taking place:—

$$\underset{\text{Dibromide of coumarin.}}{C_9H_6O_2,Br_2} + KHO = \underset{\text{Bromocoumarin.}}{C_9H_5BrO_2} + KBr + H_2O.$$

When this process is employed the dibromide of coumarin is powdered and suspended in alcohol, and rather more than enough alcoholic potash is added than is required to complete the above reaction. The decomposition takes place rapidly, the mixture becoming quite hot, and of a pale yellow colour. After it has stood for some time water is gradually added, until it ceases to throw down any more bromocoumarin. When sufficiently diluted the product is collected upon a filter, washed,

dried, and crystallised from spirit. In this way it is generally obtained in transparent needles, about half-an-inch in length. An analysis of this product gave the following numbers:—

·4102 of substance gave
·7242 of CO_2, and
·0872 of H_2O.

	Theory.		Exp.
C_9	108	48·00	48·15
H_5	5	2·22	2·36
Br	80	35·56	—
O_2	32	14·22	—
	225	100·00	

The alkaline filtrate from the above contains a quantity of this substance in solution, which may be precipitated with acid, and if a large excess of alkali has been used, most of the bromocoumarin will be found in solution; it is, however, apparently not usually so pure as that precipitated with water, and generally forms smaller crystals.

From the difference in the appearance of the products obtained by the above processes, I was at first inclined to think they were isomeric forms of bromocoumarin, but as the melting points are nearly identical, as are also the products of decomposition, I am induced to believe that these variations are due to the presence of small amounts of impurities.

α Bromocoumarin, when left in contact with cold alcoholic ammonia, decomposes with formation of ammonic bromide, and a non-crystalline sticky mass easily soluble in water. Heated with potassic hydrate it yields potassic bromide and a new acid. It decomposes when heated with potassic cyanide and alcohol in a sealed tube, forming a brown solution, from which water throws down a drab coloured amorphous precipitate. When it is heated with alcohol to 200° C. in a sealed tube for five or six hours, slight decomposition takes place, with formation of hydrobromic acid. A similar change takes place if water be used instead of alcohol.

α. *Dibromocoumarin.*

The method I previously gave for the preparation of this body consisted in heating in a sealed tube to 140° C. a mixture

of one part of coumarin, two parts of bromine, and four or five parts of disulphide of carbon. I have since found, however, that this process is greatly improved by the addition of iodine to the mixture, as it is then only necessary to heat the sealed tube for four or five hours in a bath of salt and water to complete the reaction. The product is freed from disulphide of carbon by evaporation, and from iodine by means of a solution of potassic iodide, and finally purified by two or three crystallisations from alcohol. A specimen prepared in this manner gave the following numbers:—

·2584 of substance gave
·3330 of CO_2 and
·0371 of H_2O.

	Theory.		Exp.
C_9	108	35·53	35·15
H_4	4	1·31	1·59
Br_2	160	52·63	—
O_2	32	10·53	—
	304	100·00	

The melting point of this substance is 183° C., and not 174° C. as I previously gave it. It is, however, not so definite as might be desired, as it generally shows signs of fusion below 183° C.

α Dibromocoumarin is easily decomposed by boiling alcoholic or aqueous potassic hydrate, with formation of potassic bromide, and the potassic salt of a new acid.

When suspended in cold alcoholic ammonia, α dibromocoumarin becomes of a pale yellow colour, and gradually dissolves with formation of ammonic bromide; on standing a crystalline product is deposited. It is volatile when heated, and evolves ammonia when treated with potash. The resulting alkaline solution does not deposit any product when acidified. It is soluble in water and crystallises in beautiful white needles.

The alcoholic solution upon evaporation yields a second crystalline body soluble in water. It cannot be volatilized without undergoing decomposition. A syrupy body is also produced.

I hope to return to the examination of these products at a future period.

β Bromocoumarin.

It will be remembered that the sodium derivative of the hydride of salicyl, when digested with acetic anhydride, yields ordinary coumarin. It therefore appeared to be of interest to treat the sodium compound of brominated hydride of salicyl in a similar manner, to see whether a brominated coumarin could be obtained.

The hydride of sodium-bromosalicyl, when submitted to the action of acetic anhydride, rapidly changes colour and dissolves, the mixture becoming quite hot. After the reaction has moderated, the product is well boiled for ten or fifteen minutes, and then poured into water, in which it sinks as a heavy oil, acetate of sodium dissolving. On distilling this oil, acetic anhydride and acetic acid first come over, then a quantity of oily product, which rapidly solidifies; the first half of this contains a large quantity of the hydride of bromosalicyl, the remaining portion, however, when crystallised from alcohol two or three times, yields colourless flat prisms, apparently rhombic. This substance gave the following numbers on analysis :—

I. ·5170 of substance gave
·9071 of CO_2, and
·1036 of H_2O.
II. ·3576 of substance gave
·6276 of CO_2, and
·0735 of H_2O.

The numbers give percentages agreeing with those required by the formula—

$$C_9H_5BrO_2,$$

as the following comparisons will show :—

	Theory.		Experiment.	
			I.	II.
C_9	108	48·00	47·84	47·86
H_5	5	2·22	2·22	2·28
Br	80	35·56	—	—
O_2	32	14·22	—	—
	225	100·00		

This substance is therefore monobromocoumarin. It is

moderately soluble in spirit, and when fused has an odour somewhat similar to that of coumarin. It greatly differs in properties from the bromocoumarin previously described. Its melting point is 160° C., or 50 degrees higher, and when boiled with alcoholic or aqueous potassic hydrate it does not decompose with formation of potassic bromide, but simply dissolves like ordinary coumarin, I have therefore termed it β bromocoumarin.

β Dibromocoumarin.

On treating the hydride of sodium-*di*bromosalicyl with acetic anhydride in exactly the same manner as for the preparation of β bromocoumarin, a beautifully crystalline product is obtained. It gave the following numbers on analysis :—

I. ·3639 of substance gave—
·4714 of CO_2 and
·0463 of H_2O
II. ·2020 of substance gave—
·2623 of CO_2 and
·0266 of H_2O.

These numbers give per centages agreeing with those required by the formula—

$$C_9H_4Br_2O_2,$$

as will be seen by the following comparison :—

	Theory.		Experiment.	
			I.	II.
C_9	108	35·53	35·33	35·41
H_4	4	1·31	1·41	1·46
Br_2....	160	52·63	—	—
O_2	32	10·53	—	—
	304	100·00		

The substance is therefore dibromocoumarin. It is rather difficultly soluble in alcohol. It crystallises in short hard needles. It is not the same body as that obtained by acting on coumarin with bromine and iodine. It melts at 176° C., and is not decomposed by boiling with a solution of potassic hydrate. I have, therefore, designated it as β dibromocoumarin.

Dichloride of Coumarin.

A solution of coumarin in chloroform absorbs chlorine gas, very minute quantities of hydrochloric acid being formed. On allowing the solution to evaporate spontaneously after the chlorine has been passed through it for an hour or two, a syrupy product is obtained very like new honey. This is the dichloride of coumarin. I have not analysed it, as there is no way of judging of its purity; but from its products of decomposition, there can be no doubt that it possesses the formula—

$$C_9H_6O_2,Cl_2.$$

On keeping, it appears to decompose; when heated, it gives off hydrochloric acid, and, on distillation, is converted into chlorocoumarin. With alcoholic potash it decomposes in the same way as the dibromide.

a. Chlorocoumarin.

When a mixture of one part of coumarin and three parts of pentachloride of phosphorus is heated in a retort placed in an oil-bath, the two bodies slowly react upon each other as the temperature rises, and when the oil has reached about 200° C., the product becomes a dark brown liquid (at a few degrees higher it is converted into a carbonaceous mass); during this reaction a volatile liquid, consisting chiefly of terchloride of phosphorus distils over. The contents of the retort after treatment with water, become a pasty mass of crystals, which is first purified by distillation, and then by several crystallisations from alcohol. The substance gave the following numbers on analysis:—

I. ·3904 of substance gave—
.8546 of CO_2 and
·1050 of H_2O.

II. ·4006 of substance gave—
·8760 of CO_2 and
·1047 of H_2O.

III. ·3364 of substance gave—
·2703 of AgCl.

These numbers give percentages agreeing with those required by the formula—

$$C_9H_5ClO_2.$$

The following is a comparison of the theoretical and experimental numbers—

	Theory.		Experiment.		
			I.	II.	III.
C_9	108·0	59·83	59·70	59·64	—
H_5	5·0	2·77	2·98	2·90	—
Cl	35·5	19·67	—	—	19·88
O_2	32·0	17·73	—	—	—
	180·5	100·00			

From these results it is evident that the pentachloride of phosphorus has simply given up chlorine to the coumarin. It is very curious that if half the amount of pentachloride of phosphorus mentioned above be employed, the product of the reaction suddenly carbonizes, sometimes when the oil-bath is at a temperature as low as 150° C. I have had this happen twice, whereas with the *excess* of pentachloride the product may be heated in an oil-bath standing at 200° C.

Chlorocoumarin may be easily prepared by treating the dichloride of coumarin with alcoholic potash in exactly the same manner as described for the preparation of α bromocoumarin, the reaction being analogous—

$$\underset{\text{Dichloride of coumarin.}}{C_9H_6O_2Cl_2} + KHO = \underset{\text{Chlorocoumarin.}}{C_9H_5ClO_2} + KCl + H_2O.$$

Obtained by either of the above processes, this substance forms flat needles about half an inch long. It is moderately soluble in alcohol, and slightly so in hot water, from which it crystallises on cooling.

It melts at 122°—123° C., and when heated emits an agreeable aromatic odour. When boiled with alcoholic potassic hydrate, it decomposes with formation of potassic chloride, and forms the same product as α bromocoumarin when treated in the same manner.

From this description, α chlorocoumarin is evidently a substance different from that obtained by Dr. Bäsecke, his product is in fact the β chlorocoumarin corresponding to the β bromocoumarin, and was obtained from the hydride of chlorosalicyl.

Tetrachlorocoumarin.

Chlorine gas, when passed through a solution of coumarin and iodine in tetrachloride of carbon, is rapidly absorbed, hydrochloric acid being evolved; if the gas be passed for two or three hours, a quantity of a reddish body separates, on evaporating the product so as to separate the tetrachloride of carbon, an oily residue is obtained, the red substance having fused with the impurities.

On mixing this substance with alcohol, it soon becomes a white paste. This is then pressed in a small linen bag, when a white product is obtained, which is further purified by being several times crystallised from spirit. It gave the following numbers on analysis :—

·3877 of substance gave—
·5309 of CO_2 and
·0355 of H_2O.

These numbers give per centages approximating to those required by the formula—

$$C_9H_2Cl_4O_2,$$

as will be seen from the following comparison :—

	Theory.		Exp.
C_9	108	38·03	37·32
H_2	2	0·70	1·02
Cl_4	142	50·00	—
O_2	32	11·27	—
	284	100·00	

It is therefore a tetrachlorocoumarin. This substance melts at 144°—145° C. It is difficultly soluble in spirit from which it crystallises in small white needles. When heated with alcoholic potassic hydrate, it decomposes, with formation of potassic chloride and the salt of a new acid not yet examined.

Coumarilic Acid.

I have already mentioned that α bromocoumarin when boiled with a solution of potassic hydrate decomposes, yielding potassic bromide and the salt of a new acid. To prepare this acid in a

pure state, I have found it best to proceed in the following manner: A quantity of pure α bromocoumarin is mixed with an excess of the ordinary solution of potassic hydrate. On heating this mixture, the bromocoumarin gradually dissolves, but on reaching the boiling-point, the solution rapidly becomes a pasty crystalline mass. Sufficient water is then added to dissolve this, and the boiling continued for about an hour. The solution on cooling, deposits the potassic salt of the new acid in small needles. If any quantity of this salt remains in the mother-liquor, the addition of potassic hydrate will precipitate it. The crystalline salt thus obtained is collected upon a linen filter and well pressed, to remove as much of the alkaline-mother liquor as possible. It is then crystallised once or twice from alcohol and dried.

To obtain the acid from this salt it is dissolved in water, and hydrochloric acid is added in excess. The new acid is then thrown down as a snow white crystalline precipitate, which is purified first by washing with water on a filter, and then by crystallisation from boiling water.

It gave the following numbers on analysis:—

I. ·2112 of substance gave—
·5146 of CO_2 and
·0734 of H_2O.

II. ·2561 of substance gave—
·6266 of CO_2 and
·0846 of H_2O.

These percentages give numbers agreeing with those required by the formula—

$$C_9H_6O_3,$$

as the following comparison will show:—

	Theory.		Experiment.	
			I.	II.
C_9	108	66·67	66·45	66·72
H_6	6	3·70	3·86	3·67
O_3	48	29·63	—	—
	162	100·00		

This acid, which I have proposed to call *coumarilic acid*, melts at 192°—193° C. It distils without leaving any residue, but decomposes partially with formation of an oily body smelling

like naphthaline. When gently heated, it sublimes. The vapour is very suffocating. It is excessively soluble in alcohol, but difficultly so in chloroform and disulphide of carbon. It is moderately soluble in boiling water, from which it crystallises on cooling in beautiful long needles like benzoic or cinnamic acid. Its aqueous solution has a bitter taste. It is not decomposed when heated with potassic hydrate to 180° C. for an hour.

α chlorocoumarin may be employed instead of α bromocoumarin in the preparation of this acid. It is monobasic.

Ammonic Coumarilate.—This salt is easily obtained by dissolving coumarilic acid in aqueous ammonia, and evaporating in vacuo over sulphuric acid. It is a beautiful salt, crystallising in flat prisms, radiating from a common centre. It is easily soluble in water.

Sodic Coumarilate.—Coumarilic acid dissolves in a solution of sodic carbonate with effervescence, forming a salt which crystallises in transparent rectangular tables. It is easily soluble in water.

Potassic Coumarilate.—The preparation of this salt has already been given. It is difficultly soluble in cold alcohol, but moderately soluble in this menstruum when boiling; nearly insoluble in solutions of potassic hydrate of about 20 per cent. It crystallises in prisms half an inch long which break up into small plates. Its taste is bitter. A determination of the potassium in this salt gave the following numbers:—

·1781 of salt gave—
·0759 of K_2SO_4 = 19·07 per cent. of potassium.

The formula $C_9H_5KO_3$ requires 19·5 per cent. of potassium.

Calcic Coumarilate is thrown down as a precipitate on addition of calcic chloride to potassic coumarilate. It is crystalline and difficultly soluble in water.

Baric Coumarilate is somewhat like the calcic compound.

Argentic Coumarilate.—On adding argentic nitrate to a solution of potassic coumarilate, this salt is thrown down as a white curdy precipitate, slightly soluble in water. The following determinations were made of the silver in this salt:—

I. ·1118 of substance gave—
·0443 silver = 39·62 per cent.

II. ·1608 of substance gave—
·0648 of silver = 40·29.

The formula $C_9H_5AgO_3$ requires 40·15. Analysis II was made from coumarilic acid prepared from α chlorocoumarin. I from α bromocoumarin.

Plumbic Coumarilate is a white curdy precipitate.

Mercurous Coumarilate is also a white precipitate.

Ferric Coumarilate is a pale brown precipitate.

Bromocoumarilic Acid.

This acid is produced in the same manner as coumarilic acid, but substituting α dibromocoumarin for α bromocoumarin. The acid is also purified by crystallisation from spirit and water instead of water. It gave, on analysis, the following numbers:—

I. ·2504 of substance gave—
·4109 of CO_2 and
·0489 of H_2O.

II. ·3260 of substance gave—
·5357 of CO_2 and
·0658 of H_2O.

These numbers give percentages agreeing with the formula—

$$C_9H_5BrO_3,$$

as the following comparison will show:

	Theory.		Experiment.	
			I.	II.
C_9	108	44·81	44·75	44·82
H_5	5	2·08	2·17	2·24
Br	80	33·19	—	—
O_3	48	19·92	—	—
	241	100·00		

I therefore propose to call this acid *bromocoumarilic acid;* its formation may be expressed thus:—

$$\underset{\text{Dibromocoumarin.}}{C_9H_4Br_2O_2} + H_2O = \underset{\text{Bromocoumarilic acid.}}{C_9H_5BrO_3} + HBr.$$

Bromocoumarilic acid melts above 250° C. It crystallises

from a mixture of spirit and water in needles. It is very soluble in alcohol, and but little so in water. When heated to 180° C. with potassic hydrate, it decomposes and becomes brown, potassic bromide being formed. It has a bitter taste, and is monobasic.

Ammonic Bromocoumarilate is easily soluble in water, and crystallises in needles.

Sodic Bromocoumarilate is easily soluble in water, but does not produce good crystals.

Potassic Bromocoumarilate.—This salt is prepared like the corresponding coumarilate. It is easily soluble in water, but is almost wholly thrown down from its aqueous solution by strong solutions of potassic hydrate. It crystallises from alcohol in beautiful long needles. Determinations of the potassium in the salt gave the following numbers:—

I. ·3215 of substance gave—
·1026 of K_2SO_4 = 14·30 per cent. of K.
II. ·1897 of substance gave—
·0600 of K_2SO_4 = 14·17 per cent. of K.

The formula $C_9H_4BrKO_3$ requires 14·00 per cent. of potassium.

Baric Bromocoumarilate may be obtained by the addition of a solution of baric chloride to the above potassic salt as a crystalline precipitate, difficultly soluble in water.

Argentic Bromocoumarilate is a white precipitate.

Plumbic Bromocoumarilate is a white precipitate.

Sulphocoumarilic Acid.

On digesting a mixture of about one part of coumarin and five parts of fuming sulphuric acid in the water-bath for an hour or two, the product will be found to dissolve perfectly in water. This, when diluted and neutralized with baric carbonate, yields, besides baric sulphate, a soluble salt which, when evaporated, crystallises in tufts of transparent prisms. This is rendered pure by recrystallisation from water. To obtain the new acid from this salt, it is dissolved in water, and sulphuric acid added in exactly the quantity necessary to precipitate all the barium as sulphate. The solution is then filtered and evaporated, first over the water-bath and then in vacuo. In this way the acid is usually obtained in needles, easily soluble in water. It has not been burnt, but from the

analysis of its salts, its formula, when anhydrous, is $C_9H_6O_2SO_3$. Determinations of its water of crystallisation gave the following numbers :—

I. ·9330 of crystallised acid lost
·1305 of water at 100° C. = 13·99 per cent.
II. ·5635 of crystallised acid lost
·0783 of water at 100° C. = 13·9 per cent.

In one experiment I obtained this acid in octahedra, which were very brilliant whilst in the mother-liquor, but became opaque as soon as exposed to the air. A determination of the water of crystallisation gave the following results :—

·3792 of substance lost
·0527 of water at 100° C. = 13·90 per cent.

This preparation when recrystallised, was deposited on the palm of needles. It is, therefore, probable that they originally crystallised with more water than is contained in the needles.

These numbers correspond with those required by the formula—

$$C_9H_6O_2SO_3 2H_2O,$$

which theoretically contains 13·74 per cent. of H_2O. The crystallised acid does not lose any more weight at 200° C. than at 100° C.

This acid, which I propose to call sulphocoumarilic acid, possesses a strongly acid and bitter taste; it is very soluble in water, and may be evaporated to a thin syrup before it shows any signs of crystallisation. It is monobasic. When its salts are mixed with an excess of alkali, a yellow solution is obtained similar in appearance to that produced by dissolving coumarin in alkali.

Ammonic Sulphocoumarilate.—This salt is obtained by evaporating a solution of the above acid, to which an excess of ammonia has been added. It crystallises in satiny needles, very soluble in water, and also soluble in alcohol.

Sodic Sulphocoumarilate.—On adding a solution of sodic carbonate to a solution of sulphocoumarilic acid, effervescence takes place, and on evaporating the resulting solution when neutral, beautiful crystals are obtained, very transparent and derived from the rhombic octahedron. It is easily soluble in water, but nearly insoluble in alcohol.

Potassic Sulphocoumarilate crystallises in flat prisms, easily soluble in water, insoluble or nearly so in alcohol.

Baric Sulphocoumarilate.—The preparation of this salt has already been given. It contains a considerable quantity of water of crystallisation, the crystals efflorescing rapidly in vacuo.

The formula is—

$$C_{18}H_{10}O_4Ba''2SO_3 5H_2O,$$

as the following results will show:—

I. 1·0232 of crystallised salt lost in vacuo—
·1067 of H_2O = 10·43 per cent., and from vacuo to 180° C.
·0279 = 2·90 per cent.

II. ·7420 of crystallised salt lost in vacuo—
·0777 of H_2O = 10·50 per cent., and from vacuo to 180.
·0198 = 2·66 per cent.

These numbers show that this salt loses four molecules of water in vacuo, the fifth being given off entirely at 180° C.

	Theory.	Experiment.	
		I.	II.
4 mol.	10·63	10·43	10·50
1 mol.	2·66	2·90	2·66

Determinations of barium in the anhydrous salt gave the following numbers:—

I. ·2456 of substance gave—
·0969 of baric sulphate = 23·20 per cent. of barium.

II. ·1192 of substance gave—
·0474 of baric sulphate = 23·38 per cent. of barium.

III. ·0994 of substance gave—
·0393 of baric sulphate = 23·25 per cent. of barium.

The formula $C_{18}H_{10}O_4Ba''2SO_3$ requires 23·34 per cent. of barium.

Combustion of barium salt containing one molecule of water.

I. ·2911 of substance gave—
·3818 of CO_2, and
·0570 of H_2O.

II. ·3850 of substance gave—
·5010 of CO_2, and
·0787 of H_2O.

These give numbers agreeing with the formula—

$$C_{18}H_{10}O_4Ba''2SO_3H_2O,$$

as the following comparisons will show:—

	Theory.		Experiment.	
			I.	II.
C_{18}....	216	35·70	35·77	35·70
H_{12}. ..	12	1·98	2·17	1·98
O_{11}....	176	29·09	—	—
Ba	137	22·65	—	—
S_2	64	10·58	—	—
	605	100·00		

Strontic Sulphocoumarilate.—This salt is easily soluble in water, and crystallises very nicely. It contains water of crystallisation, becoming opaque at 100° C., the last quantities of water not being expelled until a much higher temperature is used.

A determination of the strontium in the anhydrous salt gave the following numbers:—

·1698 of substance gave—
·0574 of strontic sulphate = 16·15 per cent. strontium.

The formula $C_{18}H_{10}O_4Sr''2SO_3$ requiring 16·27 per cent.

·0769 of a second specimen, dried at about 110° C., gave ·0253 of strontic sulphate = 15·69 per cent. of strontium.

The formula $C_{18}H_{10}O_4Sr''2SO_3$, H_2O requiring 15·75 per cent.

Disulphocoumarilic Acid.

On heating a mixture of about eight parts of fuming sulphuric acid and one part of coumarin to a temperature of 150° or 160° C. for an hour or two, the product contains two sulphoacids, viz., sulphocoumarilic and disulphocoumarilic acids. On treating this with baric carbonate in the usual manner, the solution contains the barium salts of these two acids. To separate them the solution is evaporated to dryness, and treated

with warm water, which removes the baric sulphocoumarilate, leaving the less soluble salt of the new acid behind. This is purified by crystallisation from boiling water, in which it is not very soluble.

Thus obtained it is a white slightly crystalline product nearly insoluble in cold water.

Dried at 100° C. it gave on analysis the following numbers:—

·3258 of substance gave—
·1648 of baric sulphate = 29·76 per cent. of barium.

The formula $C_9H_4O_2Ba''2SO_3,H_2O$ requires 29·85 per cent. of barium.

Determinations of water of crystallisation—

I. 1·4226 of salt dried at 100° C. lost
·0486 of H_2O at 180° C. = 3·42 per cent.
II. ·5612 of salt dried at 100° C. lost
·0235 of H_2O at 180° C. = 4·18 per cent.

The above formula requires 3·92 per cent.

Determination of barium in anhydrous salt—

·1904 of substance gave
·0994 of baric sulphate = 30·7 per cent.

The formula $C_9H_4O_2Ba''2SO_3$ requires 31·06 per cent.

From what has been said of the bromine and chlorine derivatives of coumarin, it is evident that the bromine or chlorine introduced must be related to different carbon groups, according as the product belongs to what has been termed the α or β derivative. In the case of the latter it is evident that it is contained in the C_6 group, as these bodies are produced from the brominated hydride of salicyl; those employed in this paper being represented thus:—

$$\left\{\begin{array}{l}COH\\C_6H_3BrHO\end{array}\right. \qquad \left\{\begin{array}{l}COH\\C_6H_2Br_2HO.\end{array}\right.$$

Hydride of bromosalicyl. Hydride of dibromosalicyl.

The bromine in the bromocoumarin obtained from these bodies by means of acetic anhydride is not attacked by boiling with potash.

In the alpha series the bromine or chlorine must be connected

with the carbon of what may perhaps be called the acetic residue. These are easily decomposed with caustic alkali.

I have endeavoured to produce a bromocoumarin of this class by employing bromacetic anhydride instead of acetic anhydride in the preparation of coumarin from the hydride of salicyl, but have not yet succeeded.

In α dibromocoumarin one half of the bromine appears to be in union with the C_6 group, the other being connected with the acetic residue, as only one atom of bromine is removed by boiling with potassic hydrate.

α Bromo- and chlorocoumarins, from their decomposition by caustic alkali, and production of coumarilic acid, would appear to to be bromide and chloride of an acid radical (coumaryl). If it were so, however, these substances should give with ammonia an amide, which would decompose on boiling with alkali, yielding ammonia and coumarilic acid; but although the substances are easily acted upon by ammonia, the product when boiled with potassic hydrate does not yield this acid. It is therefore possible that coumarilic acid is not a true acid containing the group COHO, but is only coumarin with one of hydrogen replaced by hydroxyl, unless some molecular change takes place during its formation; and it is perhaps worth remarking that coumarin and its bromine, chlorine, and sulphuric derivatives give yellow solutions with caustic alkali, whereas coumarilic acid forms colourless ones; this may perhaps point to a change in structure. I hope, however, to replace the hydroxyl in coumarilic acid by bromine, and see if the resulting compound is ordinary α bromocoumarin.

Fittig and others consider coumarin as the anhydride or glycollide of oxycinnamic acid, and it appeared to me probable that if it were so it should yield with phosphoric chloride the chloride of chlorocinnamyl. I have not, however, as yet succeeded in obtaining this body, chlorocoumarin being the principal product found.

I must say that if coumarin be a glycollide it is a very anomalous one in its properties, as it may be kept *dissolved* in caustic alkali for months without formation of any appreciable quantity of coumaric acid; neither does it form an amide when heated alone in gaseous ammonia, or in a sealed tube with alcoholic ammonia; whereas salicylide, the glycollide of salicylic acid, is converted into a salicylate as quickly as it dissolves in

an alkali, and from the description given it would appear that it cannot exist in *solution* in alkali.

Coumarilic acid differs in composition from coumaric acid by H_2, and from melilotic and phloretic acids by H_4, so that we have the following series :—

$C_9H_6O_3$ coumarilic.
$C_9H_8O_3$ coumaric.
$C_9H_{10}O_3$ melilotic and phloretic.

These acids are, however, very different in properties; for example, phloretic and melilotic acids distil with formation of their anhydrides, and coumarilic acid distils with only partial decomposition, whereas the intermediate compound, coumaric acid, when heated, forms a brown resinous mass, and when distilled is entirely split up; if coumarin were its anhydride, we should expect it to be produced, especially as it is very stable and easily volatilized.

The following is a list of the new products described in this paper :—

Dibromide of coumarin	$C_9H_6O_2,Br_2$.
Dichloride of coumarin	$C_9H_6O_2Cl_2$.
α. Bromocoumarin	$C_9H_5BrO_2$.
β. Bromocoumarin	$C_9H_5BrO_2$.
α. Chlorocoumarin	$C_9H_5ClO_2$.
β. *Chlorocoumarin*	$C_9H_5ClO_2$ (*Bäsecke*).
α. Dibromocoumarin	$C_9H_4Br_2O_2$.
β. Dibromocoumarin	$C_9H_4Br_2O_2$.
Tetrachlorocoumarin	$C_9H_2Cl_4O_2$.
Coumarilic acid	$C_9H_6O_3$.
Bromocoumarilic acid	$C_9H_5BrO_3$.
Sulphocoumarilic acid	$C_9H_6O_2SO_3$.
Disulphocoumarilic acid	$C_9H_6O_22SO_3$.

V.—*On the Action of Sulphuric Acid on the Natural Alkaloids.*

By Henry E. Armstrong.

The experiments, the results of which are given in this paper, form part of a series commenced in conjunction with the late lamented Dr. Matthiessen.

The action of sulphuric acid on the natural alkaloids was first made the subject of investigation by Arppe, who in 1845 shortly described a body obtained from morphine, to which he gave the formula—$4(C_{35}H_{40}N_2O_6) + 5SO_3$. Laurent and Gerhardt (Ann. Ch. Phys. [3] xxiv. 112) led by their researches on the Amides and Anilides to doubt the correctness of this formula—which, if true, would imply that a reaction had taken place entirely without analogy—reinvestigated the matter further, including both morphine and narcotine in their experiments. From the results obtained, they considered the composition of the bodies which they succeeded in preparing, to be represented by the formulæ $C_{34}H_{36}N_2O_8S$ and $C_{46}H_{48}N_2O_{16}S$, and termed them respectively *sulphomorphide* and *sulphonarcotide*, looking upon them as derived from the neutral sulphates of the bases by abstraction of the elements of 2 mols. OH_2:

$$2C_{17}H_{19}NO_3,H_2SO_4 - 2OH_2 = 2C_{17}H_{18}NO_3,SO_2.$$
$$2C_{23}H_{25}NO_7,H_2SO_4 - 2OH_2 = 2C_{23}H_{24}NO_7,SO_2.$$

They considered them, in fact, to be true amides, and as bearing the same relation to the neutral sulphates of the respective bases, as sulphamide and sulphanilide bear to the neutral sulphates of ammonia and aniline. They were unable also to separate a base from the narcotine compound by the action of potash, and this seems to have further strengthened them in their opinion as to its constitution.

By the action of sulphuric acid on codeine, they obtained a body identical with it in composition, to which they gave the name of modified or amorphous codeine.

The light thrown on the constitution of the organic bases by the researches of Dr. Matthiessen and others, rendered it highly improbable that the above-mentioned bodies were constituted as supposed by Laurent and Gerhardt, and even allowed a speculation as to their probable nature: for the dis-

covery of apomorphine at once seemed to point to the possibility of the morphine product being none other than the sulphate of that base, especially as the description of its properties agreed moderately well with those characteristic of apomorphine. Their identity was proved by Drs. Matthiessen and Wright, who succeeded in isolating apomorphine from the product of the reaction of dilute sulphuric acid on morphine in sealed tubes at 100°. This rendered an analogous constitution of the narcotine and codeine products probable, a surmise which has, however, not been confirmed by experiment.

On heating narcotine with an excess of acid of the strength of equal volumes of ordinary concentrated sulphuric acid and water, in an open porcelain dish on a water-bath, it is observed that the colour of the mass gradually darkens, and that after a time, and almost suddenly, the whole becomes of a dark pink colour. It is then thrown into a considerable quantity of warm water, in which it entirely dissolves, and a slight excess of ammonia is added, which throws down the base as an amorphous, almost white precipitate. This was brought on a filter and washed with warm water. It was found to be very easily soluble in alcohol, insoluble in carbonate of soda, readily soluble in potash, and when heated under water to cake together in the form of a sticky semi-fluid mass. This behaviour at once suggested the probable nature of the base; for all the above properties agree with those exhibited by the first product of the action on narcotine, viz., dimethylnornarcotine; and a further examination soon proved this to be really the case. The product was purified by solution in hydrochloric acid; addition of sodic carbonate in excess to remove any monomethylnornarcotine, which is soluble in the latter reagent; redissolution in hydrochloric acid; and addition of potash in excess, which dissolves dimethylnornarcotine, leaving any nornarcotine or narcotine undissolved. The alkaline solution was then neutralised with hydrochloric acid, and ammonia was added; the base so obtained and dissolved in hydrochloric acid, precipitated by sodic carbonate, was extracted with ether; the ether shaken up with hydrochloric acid; the hydrochloric acid solution precipitated with ammonia; and the base after washing dried at 100° and analysed.

1. ·4917 grm. gave ·2332 grm. OH_2 and 1·1397 grm. CO_2.
2. ·366 grm. gave ·1724 grm. OH_2 and ·8455 grm. CO_2.

	Calculated.		Found.	
			I.	II.
C_{21}	252	63·16	63·2	63·1
H_{21}	21	5·26	5·2	5·24
N.....	14	3·51	—	—
O_7	112	28·07	—	—
$C_{21}H_{21}NO_7$	399	100·00		

The above analyses prove beyond doubt the identity of the base with dimethylnornarcotine.

The conversion of the narcotine was perfect, and if the reaction was arrested immediately on the appearance of the pink colour throughout the whole mass, an almost pure product was obtained, as is shown by the following analysis of the crude product obtained by directly precipitating the base with ammonia and washing with warm water:—

·54 grm. gave ·265 grm. OH_2 and 1·247 grm. CO_2; whence C = 63·0 per cent., H = 5·4 per cent.

The reaction has therefore taken place according to the equation:—

$$C_{22}H_{23}NO_7 + H_2SO_4 = C_{21}H_{21}NO_7 + CH_3HSO_4.$$

The methylsulphovinic acid formed is again decomposed into sulphuric acid and methyl alcohol: for on adding baric carbonate in excess, filtering and evaporating to dryness, no baryta salt was obtained.

For the complete conversion of 50 grms. narcotine, I have found it necessary to heat between two and three hours. If the heating be continued beyond the above-mentioned point, a second atom of methyl can be removed, and probably a third; but a very impure product is obtained, sulphurous anhydride is given off, and partial carbonisation takes place.

By the analysis of a crude product obtained by further heating, &c., the following results were obtained:—

·4125 grm. gave ·1945 grm. OH_2 and ·937 grm. CO_2; therefore C = 61·9 per cent.; H = 5·2 per cent.

It is probable that the substance analysed by Laurent and Gerhardt was a mixture of the sulphates of di- and mono-methylnornarcotine. That they should have been led to consider it an amide and not the sulphate of a base, evi-

dently arises from the fact that dimethylnornarcotine is soluble in potash, and that on the addition of an acid, the respective salt is precipitated and only dissolved again on addition of a large quantity of water. On treating their product with nitric acid, they obtained a yellow substance soluble in ammonia, and of course were able to detect sulphuric acid in the solution, whereas if the pure substance prepared as above is similarly treated, the yellow body is obtained, which is perhaps a nitro substitution product, but not a trace of sulphuric acid can be detected.

On treating codeine in a similar manner, and heating until the precipitate produced by sodic carbonate did not visibly increase; then dissolving the product in water, precipitating with sodic carbonate, redissolving in hydrochloric acid, and reprecipitating with sodic carbonate, which operation was twice repeated in order to remove any codeine,—then extracting with ether and shaking up the ether with concentrated hydrochloric acid, a crystalline hydrochlorate was obtained, which, on analysis, gave numbers agreeing very well with those calculated for hydrochlorate of codeine.

I. ·517 grm. gave ·309 grm. OH_2 + 1·2162 grm. CO_2.
II. ·5725 grm. „ ·3423 grm. OH_2 + 1·3558 grm. CO_2.
III. ·2257 grm. „ ·0905 grm. AgCl.

	Calculated.		Found.		
			I.	II.	III.
C_{18}	216	64·38	64·15	64·58	—
H_{22}	22	6·26	6·64	6·64	—
NO_3....	62	—	—	—	—
Cl	35·5	10·5	—	—	10·4

A platinum salt was prepared and analysed with like result. ·552 grm. gave ·1067 Pt = 19·32 per cent. Pt.

$2C_{18}H_{21}NO_3HCl,PtCl_4$ requires 19·5 per cent.

The first product of the action of sulphuric acid on codeine is therefore a body isomeric therewith. Its properties are as follows:—The base falls down as a snow-white, amorphous precipitate on the addition of sodic carbonate. (Codeine is only precipitated after some time from concentrated solutions and always crystalline.) The hydrochlorate crystallises in groups

of apparently hexagonal pyramids radiating from a common centre, and differs from the corresponding codeine hydrochlorate by losing both its molecules of water of crystallisation at 100°, whereas the former loses only $\frac{3}{4}$ at 100°, the remaining $\frac{1}{4}$ only being expelled at 120°. The platinum salt is quite amorphous and may be obtained anhydrous by drying at 100°, whereas the platinum salt of codeine is crystalline, and does not lose the whole of its water of crystallisation below 100°. The amorphous platinum salt contains 1 mol. water of crystallisation, which it loses even by prolonged exposure over sulphuric acid. Gerhardt's description of the base, &c., differs from mine, inasmuch as he says that not only the base, but all its salts are amorphous.

By the further action of sulphuric acid I have evidence that first 1 mol. OH_2 is removed from 2 mols. of codeine, an intermediate compound between codeine and apocodeine being produced, a sort of anhydride in fact; and then 1 mol. OH_2 from 1 mol. codeine; and I believe that by its further action on this apocodeine, apomorphine is formed, *i.e.*, CH_3 is removed. I am, however, not yet certain as to the exact conditions under which the first of these changes takes place, and the products being amorphous, it is extremely difficult to obtain a satisfactory separation.

With regard to morphine, I have as yet unfortunately not had sufficient quantities of material to work on to enable me to speak with certainty, but I think it probable that it is first converted into such an isomeric modification as codeine, and that also an intermediate compound exists between it and apomorphine, and derived by abstraction of OH_2 from 2 mols. of morphine.

By the action of sulphuric acid on other bases I have obtained entirely negative results; neither strychnine nor papaverine is in the least affected by it, even after many hours' digestion.

It will be interesting to extend the investigation to those alkaloids known to contain the methyl group, such as brucine and caffeine; and with these I have already commenced experiments.

VI.—*On an Alkaloïd from Cinchona Bark hitherto Undescribed.*

By David Howard.

In experimenting upon impure crystallisations of quinine salts obtained from the mother-liquors of the manufacture of sulphate of quinine, I have occasionally been perplexed by an unusual loss in recrystallising, which the mechanically adhering mother-liquor did not seem to account for.

A more careful examination of some of these substances, shows that the cause, in some cases at least, is the presence of an alkaloïd hitherto undescribed, the extreme solubility of the salts of which, both distinguishes it at once from the cinchona alkaloïds already known, and renders it very difficult to separate from the uncrystallisable quinoïdine.

The most convenient method of obtaining it, is to purify the alkaloïds contained in the mother-liquor from the recrystallisation of such impure products as I have mentioned, by solution in ether, and after evaporation of the ether to dissolve with oxalic acid in as small a quantity of water as possible, and allow it to crystallise.

The oxalate thus obtained may be purified by recrystallisation from water, with addition of animal charcoal, but I have never been able to free it entirely from a yellow colour.

The most satisfactory salt for analysis is the platino-chloride, which is prepared in the usual manner; it is almost insoluble in water or in cold hydrochloric acid, but soluble with difficulty in hot strong acid; it forms a crystalline powder by precipitation, and well defined crystals by solution in acid.

The analysis shows that it is isomeric with the platino-chloride of quinine, but anhydrous, instead of containing one atom of water of crystallisation, given off at 120°, as does the salt of quinine.

The ultimate analysis for which, as well as for the other combustions which I shall have to mention, I am indebted to the skill of Mr. Huxley and Mr. Gray, of the Royal College of Chemistry, gives the following results:—

	C.	H.	Pt.
Experiment I.....	32·67	3·67	26·63
,, II	32·67	3·82	26·62

Gerhardt's formula for the anhydrous platino-chloride of quinine, $C_{20}H_{24}N_2O_2$, 2HCl, $PtCl_4$ requires

C 32·60 H 3·53 Pt 26·76.

The salt taken for analysis was precipitated from a hot acid solution, and was a distinctly crystalline powder.

The composition is the same whether it be precipitated cold in a

neutral solution, or crystallised from a strong acid solution, as the following results will show:—

Platino-chloride precipitated cold, Pt 26·50
do crystallised 26·62

The oxalate, as I have before mentioned, though it is the most easily crystallised of the salts of this alkaloïd, is unfortunately very difficult to purify entirely, and changes so readily under the influence of air, light, or heat, that I have been unable to obtain it colourless. When a dilute aqueous solution is concentrated by evaporation in a water-bath, the change of colour shows that decomposition has to a certain extent taken place, and on the addition of water, a brown resinoïd matter separates from the solution. To find out if this was caused by impurities or was a property of the salt itself, I decomposed the platino-chloride of known purity by several processes, but in each case the resulting oxalate had the same colour and the same tendency to decompose. Even when prepared from perfectly colourless solutions of the alkaloïd in ether, I have still found the oxalate of a greenish-yellow hue, even before the application of heat; in fact, I am not sure that this colour may not be inherent in the salt itself.

It is extremely soluble in water, the wet crystals melting at 100°, but much less so in cold water; insoluble in ether, but very soluble in alcohol, and to a less degree in amylic alcohol, from hot concentrated solutions in either of which menstrua, it crystallises freely on cooling. The water of crystallisation is partially given off in vacuo, and entirely at 100° after previous drying; if the salt is at once heated to 100° without previous exsiccation, it is apt to fuse.

The combustion proved exceedingly difficult; the usual process with cupric oxide was found inadmissible, the oxalate assuming a dark brown colour as soon as it touched the oxide. The only practicable method is burning in oxygen gas, and even in this mode of analysis, the low temperature at which the substance partially decomposes, makes it difficult to accomplish successfully. It will be seen that the results, though agreeing very closely among themselves, differ considerably from the probable formula, showing plainly the difficulty of obtaining a pure product.

The hydration and the oxalic acid point to the formula $2(C_{20}H_{24}N_2O_2),C_2H_2O_4 + 9aq.$, the numbers obtained being:—

	C.	H.	$C_2H_2O_4$.	H_2O at 100.	H_2O in vacuo.
Theory ..	56·00	7·55	10·00	18·00	
Exp. I ..	57·57	8·64	10·07	17·98	14·23
„ II ..	57·42	8·74	9·98	17·98	14·09
„ III .	57·74	9·14	10·08	17·89	14·02
„ IV .	57·85	8·79	10·23	17·72	13·82
„ V ..	—	—	10·19	17·98	—

The water lost by drying in vacuo agrees very closely with 7 atoms, viz., 14·00 per cent.

The salt thus differs from oxalate of quinine by 3 atoms of water of crystallisation, the formula of the latter being $2(C_{20}H_{24}N_2O_2),C_2H_2O_4, + 6aq$.

The properties of the other salts which I have examined are as follows:—The sulphate, tartrate, citrate, hydrochlorate, phosphate, and acetate are all exceedingly soluble in water; on evaporation in vacuo they form semi-crystalline masses, impossible to obtain in a state fit for analysis.

The hydrobromate and ferrocyanide obtained by double decomposition form oily strata at the bottom of the solution, soluble in an additional quantity of water, but even on long standing they show no sign of crystallisation.

The hydriodate also forms an oily stratum in strong solutions, but on standing it becomes semi-solid by the formation of crystals; weaker solutions also deposit a small quantity of flocculent crystals, but in neither case can they be separated from the mother-liquor.

The sulphocyanide, while also forming an oil when in concentrated solutions, crystallises from a somewhat larger quantity of water in long silky needles, almost white, very soluble, and readily decomposed by heat.

The iodo-sulphate I have not as yet succeeded in forming. I much regret this, on account of the great importance of this salt in the cinchona alkaloïds, and further experiments are needed, either to form it or to prove its absence.

The alkaloïd itself, as obtained by precipitation from a solution of its salts by potash or soda, is a yellowish oil. I have not been able to obtain it pure in the solid state, for it will not bear heat without decomposition, and holds water too strongly to dry in vacuo. It is very soluble in alcohol, soluble to a large extent in ether, from which it separates as an oil when the ether is allowed to evaporate. It is a strong base; the salts are neutral to test-paper; a small excess of the base strongly restores the colour of reddened litmus. Ammonia precipitates its solutions but imperfectly, and, if we may judge from this it is even a stronger base than quinine.

Chlorine-water followed by ammonia, produces in solutions of its salts the green colour and precipitate of dalleiochin which distinguishes quinine and quinidine. Strong acids, even in the cold, produce a change of colour, and even when diluted with a considerable quantity of water; heat renders the action much more rapid. This coloration is strongest when nitric acid is used, an excess of which, with the aid of heat, will develope a strong yellow-green colour, even in a weak solution. In this reaction, as well as in the persistent colour of its salts, this alkaloïd shows a curious resemblance to aricine.

The yellow colour renders the examination of its optical properties difficult, but, as far as has been hitherto tried, it is inactive. I have not been able to recognize fluorescence in its solutions.

Its taste is a peculiar bitter, very much less, both in intensity and permanence, than that of the other cinchona alkaloïds.

I have not been able to find out whether this alkaloïd is contained in all the species of cinchona, or, if not, to which it belongs, for the difficulty of the crystallisation of the impure salts makes it a matter of uncertainty to obtain it.

My uncle, Mr. J. E. Howard, when investigating the leaves of the *Cinchona Succirubra*, from India, found minute quantities of an alkaloïd, soluble in ether, from which an alcoholic solution of oxalic acid precipitated it in a crystalline form; but the small quantities at his disposal prevented his examining it further than to show its analogy with quinine; his present conviction is that this substance is identical with the alkaloïd I have been describing, and though the evidence is not yet sufficient to enable us to speak with certainty, it tends strongly to prove it. It seemed so desirable to settle this point, and to throw some light, if possible, on the order of formation, and possibly on the far more important and far more difficult question of the mode of formation of the alkaloïds of the descending sap, that he has written to Mr. Broughton, and we hope shortly to receive a quantity of the leaves sufficient to enable us to investigate it.

VII.—*On the Origin of Nitrates in Potable Waters.*

By Charles Ekin, Bath.

I have frequently been at a loss to account for the presence of considerable quantities of nitric acid in potable waters, where contamination by sewage or manured land was out of the question. To give but one instance, there is a hill near Bath, capped by the Great Oolite, which has not a single house upon it, no drainage near it, and on whose scanty herbage browse only a few sheep, and yet the springs rising at the junction of the Oolite with the Fuller's earth contain as much as ·65 grains of nitric acid per gallon. Here, then, after making all due allowance for the combined nitrogen contained in rain water, which, according to the observations of Lawes, Gilbert, and Way, amounts to ·24 parts nitrogen in 1,000,000, there still remains the large proportion of eight to one to be accounted for. And this proportion will be still further increased if we consider that much of the nitric acid and ammonia

present in rain water must be absorbed by vegetation in its passage through the soil.

It has, of course, long been known that water from artesian wells in the chalk contains nitrates which cannot possibly be referred to sewage or other impurity, but I am not aware that it has been suspected that other strata might also contain nitrates. It was to ascertain this in the absence, so far as I know, of any published experiment bearing on the subject, that the following experiments were made, and to ascertain, if possible, the origin of these nitrates which, according to Dr. Paul, in his comprehensive article on Water Analysis, in Watts's Dictionary of Chemistry, has not yet been done.

The rocks and fossils mentioned below were all most carefully collected by myself from situations where any accidental contamination seemed impossible, none of them having been exposed to the weather or to percolating impurity.

The method I pursued was to powder the fossils roughly, and macerate them for a few days in perfectly pure distilled water; to pour off the clear supernatant liquid; add an equal quantity of solution of pure sodium hydrate (1 to 10); transfer to a retort; dissolve in the liquid a piece of thin sheet aluminium; collect the ammonia by distillation; and estimate it by Nessler's test.

The utmost care was used to insure the purity of the water and solution of sodium hydrate, and perfectly negative results were obtained in each case by blank experiments.

Proceeding in this way, I found that grey chalk marl contained 1·1 part of combined nitrogen in 1,000,000 parts; Bath oolite, 1·3 parts; fossils from the Green-sand, 2·23 parts; fossils from the Lias, 3·6 parts; another sample of fossils from the Lias, 4 parts; fossils from the Fuller's earth, nearly 3 parts; a sample of Inferior Oolite rock, 7·6 parts; and another sample of the same, 6·9 parts. The samples of Inferior Oolite rock were entirely made up of fossils, and although I had every reason to trust the results given by my first experiment, yet the quantity of nitrogen present was so high that I obtained the second sample from a different locality, but it gave almost the same results. The high figure of combined nitrogen given by the Inferior Oolite caused me to look at my note-book, and I found that almost without exception the springs in this neighbourhood which I have examined, and which had percolated through the Inferior Oolite, rising at its junction with the Lias, contained a larger quantity of nitric acid, varying from 1½ grain to 2 grains per gallon, than the springs rising at the junction of the Great Oolite with the Fuller's earth, and this I attribute to the one stratum being so much more fossiliferous than the other.

It is still the practice of many of our first analysts to look with great suspicion upon waters containing any appreciable amount of nitric acid,

but that this nitric acid is not necessarily due to the oxidation of excretal matter, I think the foregoing experiments sufficiently prove, and I venture to think in consequence that the "previous sewage contamination theory" ought to be considerably modified.

VIII.—*On the Development of Fungi in Potable Water.*

By E. Frankland, Ph.D., D.C.L., F.R.S.

In June, 1870, Mr. Heisch communicated to the Chemical Society the results of some very interesting observations on the development of cellular and fungoid growths, in various waters to which a small quantity of crystalline sugar had been added. Having observed this phenomenon in water to which sewage was strongly suspected to have gained access, he procured water from various sewers, and after allowing the suspended matters to settle, six drops of each sample of clarified liquid were mixed with 10,000 grains of West Middlesex and New River water, and to 6 oz. of each sample, thus polluted, 10 grains of pure sugar were added, a like quantity being mixed with 6 oz. of the water without the sewage. All the samples were placed in stoppered bottles in a window where plenty of light could reach them. It was found that the water and sugar remained clear and sweet, as did also the water and sewage without sugar; but the mixtures of water sewage, and sugar became turbid, and on being submitted to microscopic examination, were found to contain small spherical cells with, in most cases, a very bright nucleus. After the lapse of some days, these cells gradually grouped themselves together in bunches something like grapes; they next spread out into strings, with a wall surrounding and connecting the cells; the original cell-walls then seemed to break, and leave apparently tubular sort of threads branched together. Mr. Heisch then describes a number of other experiments which, taken together with the foregoing, led him to the conclusion, that the cells of these germs, when thus developed, are distinct evidence of sewage contamination, and that the germs producing these cells are not removed by filtration through the finest Swedish paper, neither are they destroyed by boiling for half-an-hour.

These remarkable results excited in myself, and doubtless in other chemists occupied in the investigation of potable waters, the liveliest interest. In connection with the most generally accepted hypothesis of the cause of the spread of epidemic disease through the agency of water, there was here discovered a much nearer approach to the supposed morbific matter in such water, than had before been attained. Another parallel was apparently opened, from which one of the strongholds of

disease could be at least reconnoitred, if not actually attacked and vanquished.

At the earliest possible moment I repeated and extended these experiments, and at the outset had the advantage of seeing in Mr. Heisch's laboratory the cells and fungoïd growth which he described in the paper already alluded to. At a subsequent stage of my inquiry, I was also much indebted to Mr. Bell of the Inland Revenue laboratory, for information about, and specimens of, various fungoïd growths, some of which are alluded to in his valuable paper on "Fungi and Fermentation," recently published in the Journal of the Chemical Society.

My own experiments completely confirm Mr. Heisch's observations, with two important exceptions, viz., that firstly, the fungoïd growths are not peculiar to water contaminated with sewage; and, secondly, the germs from which they originate are present in all water, which has been, even momentarily, in contact with the air. Samples of water which, when mixed with the proportion of sugar which he recommends, remained clear and transparent for weeks, rapidly became turbid when a few drops of sewage were added to them; and the consecutive development of clusters of cells and threads occurred exactly as he describes. One drop of fresh urine in 10,000 grs. of water soon produced crowds of cells and, at a later period, mycelial threads. Samples of effluent water from meadows irrigated with sewage, when mixed with sugar, presented perfectly similar phenomena, as did also samples of well water, yielding the following results on analysis:

Results of Analysis expressed in parts per 100,000.

Description.	Total solid impurity.	Organic carbon.	Organic nitrogen.	Ammonia.	Nitrogen as nitrates and nitrites.	Total combined nitrogen.	Previous sewage or animal contamination.	Chlorine.	Hardness.			Remarks.
									Temporary.	Permanent.	Total.	
Sultan's Row Well, East Retford	188·84	·935	·106	·161	4·384	4·603	44850	23·70	7·71	23·94	31·65	Yellow, clear.
Orchard Well, Crathorne, West Yarmouth, 5 ft. deep to water; total depth, 8 ft.	123·92	·442	·101	·027	1·637	1·760	16270	12·50	6·45	36·15	42·60	Slightly turbid.
Jacob's Well, Sheffield	18·50	1·200	·126	·110	0	·217	590	2·20	2·03	1·35	3·38	Offensive, swarming with vibrios and bacteria.
Pump in Sheep Street, Cirencester	55·88	·332	·074	·036	·802	·906	8000	5·10	26·66	8·34	35·00	Very turbid.

Samples of water taken from the Thames above Streetley and below Reading, and from the Kennet below Reading, also gave, under the same conditions, fine mycelial growths. On the other hand, the water delivered by the eight London Water Companies gave, in but one or two cases, slight evidence of cellular or mycelial development, whilst the following samples exhibited, even after several weeks' contact with sugar, no signs of the characteristic cells and fungi, nor indeed of any other organisms :—

Results of Analysis expressed in parts per 100,000.

Description.	Total solid impurity.	Organic carbon.	Organic nitrogen.	Ammonia.	Nitrogen as nitrates and nitrites.	Total combined nitrogen.	Previous sewage or animal contamination.	Chlorine.	Hardness.			Remarks.
									Temporary.	Permanent.	Total.	
Deep chalk well water at Canterbury, softened by Clark's process	11·94	0	0	0	·431	·438	3990	2·10	·69	4·17	4·86	Clear.
Cerney Springs, Thames Head	33·86	·052	·016	·001	·282	·299	2510	1·30	22·76	3·88	26·64	
Shallow Well, near top of Harrow Hill	53·92	·078	·027	·004	·057	·087	280	8·90	10·37	21·78	32·15	Clear.
Well in chalk, 340 feet deep, furnishing Harrow water supply	100·88	·059	·030	·118	0	·127	650	16·30	18·98	25·42	44·40	Clear.
Water from bore hole in Bushey Meadows, near Watford, 130 feet deep	33·88	·027	·006	·006	·314	·325	2870	1·35	23·77	3·77	27·54	Clear.
Chalk well, 378 feet deep, presented to Stoke Row by the Rajah of Benares, 510 feet above sea	29·20	·052	·024	0	·059	·083	270	1·18	21·91	3·51	25·42	Clear.
Deep chalk well at Gallows Tree, near Reading, 250 feet above Thames	23·30	·051	·017	·001	·105	·123	740	1·00	16·41	2·73	19·14	Clear.

Thus far my results were quite in harmony with those of Mr. Heisch, and in accordance with what might be anticipated from a knowledge of the sources of the waters and of their previous history as revealed by chemical analysis ; but I now encountered some reactions which at first puzzled me exceedingly. The first of these was the following :—

During a visit to Mr. Hope's new irrigation farm at Romford on the 26th of November last, I collected a sample of effluent water from one of the drain outfalls. This water consisted of the sewage of Romford which had percolated to the tile drains through some four or five feet of loose gravelly soil. It was clear, but that it still contained a considerable proportion of unoxidized sewage was evident, from the following results which it yielded on analysis—

100,000 parts contained:—

Total solid impurity in solution	85·60
Organic carbon	·844
Organic nitrogen	·233
Ammonia	·040
Nitrogen as nitrates and nitrites	1·143
Total combined nitrogen	1·419
Chlorine	9·30
Temporary hardness	27·95
Permanent ,,	20·60
Total ,,	48·55

The proportion of organic carbon was three times, and that of organic nitrogen ten times as great as that found in unpolluted water, whilst the comparatively large proportion of ammonia showed that the oxidation of the organic matters was still incomplete. Nevertheless this water, when mixed with the proper proportion of sugar, and maintained at a temperature of about 70° Fahr. remained perfectly transparent for weeks. The result of the next experiment was still more remarkable. Two samples of the Grand Junction Company's water were mixed with sugar in the usual way; one of them was drawn from a foul uncovered cistern over and within a water-closet; the other from a clean slate cistern, in passing out of which the water filtered through some 30 or 40 lbs. of animal charcoal. The water from the foul cistern remained transparent for weeks, whilst that drawn from the clean cistern through animal charcoal soon became turbid, and in three days had produced abundant fungoid growths. Remembering Mr. Heisch's statement that filtration through *well aired* animal charcoal, is effectual in preventing these growths even in foul water, I now passed a rapid current of air through the filter for about 15 minutes, and then left it exposed to air for six hours. The result, however, was the same as before: Grand Junction water drawn through it, immediately after aëration, behaved exactly as before when mixed with sugar. These experiments seemed to indicate that the presence of a phosphate was in some way connected with the production of the fungoïd growths and other living organisms; for it is known that water dissolves traces of calcic phosphate from animal charcoal; and this supposition was strengthened, when it was found that the effluent water from the sewage farm at Romford contained no detectable trace of phosphoric acid, the plants and poor soil of this newly cultivated farm having doubtless removed all phosphates from the percolating sewage. The hypothesis of the dependence of the fungoïd and other growths upon the presence of phosphates was further supported by the results of the following experiments—

1. A sample of the Grand Junction Company's water mixed with sugar, remained perfectly clear for twelve days; minute quantities of ammonic nitrate and phosphate were now added. Three days later it swarmed with very active vibrios and cells, with bright nuclei, subsequently very luxuriant branched fungoïd threads developed themselves, and the mixture emitted a strong ferment odour, which a few days later became horribly offensive.

2. A sample of the Southwark Company's water, mixed with sugar, remained for 19 days perfectly clear and transparent; small quantities of ammonic nitrate and phosphate were then added. In a few days it was crowded with vibrios and monads; and later, it was found to contain the characteristic mycelial fibres.

3. The usual proportion of sugar was added to a sample of water which I collected at the Cerney Springs, near Cirencester; it remained clear for eight days, and was then mixed with traces of ammonic nitrate and sodic phosphate; it continued turbid ever afterwards, and soon became filled with swarms of vibrios and fine branching tubular fungoïd threads; the water subsequently became brownish, and emitted a very offensive odour.

These experiments show that potable waters which stand the sugar test perfectly, become entirely changed in their behaviour with this test, when they are mixed with traces of ammonic nitrate and sodic phosphate, and the following experiments prove that it is the phosphoric salt which alters their behaviour in this respect.

4. A sample of the Lambeth Company's water, after admixture with sugar, remained perfectly clear for 19 days; ammonic nitrate was then added; after the lapse of several weeks the clearness of the sample had not been disturbed.

5. Canterbury deep well water, softened by Clark's process, remained perfectly clear during 23 days after admixture with sugar; traces of nitrate of ammonia were then added, but, after the lapse of two months it was still perfectly transparent and unchanged.

6. A sample of the New River Company's water, after being mixed with sugar, remained perfectly clear for 19 days; ammonic nitrate was then added, but, during a further period of 12 days, no change took place.

7. The water of the shallow well at Harrow, above alluded to (p. 68), was mixed with sugar, and remained perfectly clear during 29 days; one drop of a fresh solution of albumin was then added to about $1\frac{1}{2}$ ounce of it. In four days it became very turbid, and, under the microscope, showed splendid branched tubular fungoïd threads filled with rounded cells, and closely resembling those developed in water with which sewage had been intentionally mixed. Cells with bright nuclei grouped together were seen in abundance, together with leptothrix

filaments. The solution of albumin, used in this and other experiments, was made by breaking open a fresh egg and rapidly transferring the white to a bottle containing about 6 oz. of pure distilled water which had been previously boiled for an hour and a half. Analysis proved this solution to contain distinct traces of phosphoric acid.

8. A sample of the Grand Junction Company's water, softened by Clark's process, was mixed with sugar, and remained clear during 19 days; ammonic nitrate was then added, but no alteration occurred during the next six days. When, however, a few very minute fragments of fresh animal charcoal were put into the water, it soon became turbid, and exhibited, under the microscope, groups of cells with bright nuclei and magnificent mycelial threads.

It is thus evident, that the addition of minute traces of a phosphate, either as sodic phosphate, white of egg, or animal charcoal, at once determines these fungoïd growths in saccharine water, which before exhibited no tendency to develop them.

An important question now presented itself Are the germs of these organisms necessarily contained only in the waters which develop fungoïd growths, or are they present in the atmosphere? The answer to this question was given by the following experiment:—

9. Small quantities of potassic chloride, ammonic nitrate, sodic phosphate, and sugar were dissolved in distilled water, previously boiled for many hours with caustic soda and potassic permanganate, and afterwards again distilled. Just before solution, the solid ingredients were strongly heated in a platinum spoon over the flame of a spirit lamp—the potassic chloride and sodic phosphate to redness, the ammonic nitrate until a considerable proportion had decomposed into nitrous oxide and water, and the sugar, until, after melting, it began to turn brown. This solution was placed in a stoppered bottle, as in all the previous experiments. After a few days' exposure to a temperature varying between 60° and 70° F., a magnificent mycelium of the characteristic description began to grow, and was soon followed by several others. Under the microscope the threads of this fungus were uniformly tubular, branched, with sparsely-distributed cells inside, and a few bulbs. There were also interspersed amongst the mycelium abundance of cells with bright nuclei, grouped together like bunches of grapes. The liquid was also crowded with very minute moving organisms, probably monads. A specimen of real sewer fungus was examined side by side with this, and found to be very similar in appearance, but more transparent and somewhat smaller.

It is thus evident that the purest water which can be obtained, in contact with the air, yields splendid crops of this sewage mycelium if it be supplied with the necessary soil; and further, that the sugar and salts just named contain all the elements necessary for its development.

Of these elements phosphorus is essential, for in a solution made at the same time, exposed to the same conditions, and containing the same substances, *minus the sodic phosphate*, no trace of mycelium or of any other organism made its appearance during the nine weeks it was under observation.

If it be true, then, that the germs of these fungoïd and other organisms be usually present in the air, and that they develop in a saccharine solution only when the latter contains a phosphate, it obviously follows that waters which are unaffected by this sugar test ought to be incapable of propagating sewer fungus when they are infected. This conclusion was completely verified on submitting it to the test of experiment.

10. Harrow deep well water (see page 68) which had remained perfectly clear for 24 days after admixture with sugar, was infected with washed sewer fungus, which I collected at Mr. Hope's irrigation farm, at Romford. After the lapse of five days, during which time it was maintained at a temperature of between 60° and 70° F., no growth or turbidity had occurred. A single drop of solution of albumin was now added; four days later the water had become very turbid, and numerous fungoïd growths had commenced at the bottom of the bottle. These, examined by the microscope, showed mycelium threads not very well developed, also leptothrix, and abundance of grouped cells with bright nuclei. No vibrios were observed. Afterwards the fungoïd growth became more abundant, but never so luxuriant as that obtained in Experiment No. 9, which surpassed all others.

11. Water from the bore-hole in Bushey Meadows (see page 68) which, after the addition of sugar, had maintained its transparency during 24 days, was infected, as in the last experiment, with washed sewer fungus. No growth took place; neither was the transparency of the water disturbed in the subsequent eight weeks, during which it was repeatedly and closely observed.

It is thus evident that the presence of germs in a sample of water is insufficient in itself to produce Mr. Heisch's reaction when sugar is added, and further, that a short (probably a momentary) contact with air is sufficient to impregnate any sample of water with the necessary germs, which develop, on the addition of sugar, only in the presence of a phosphate. The reaction is in fact an exceedingly delicate test for phosphoric acid. It would probably defy the powers of the most expert chemist to detect, in two ounces of water, the phosphoric acid introduced by the addition of a single drop of a dilute solution of albumin, yet these atmospheric germs find it out, appropriate it, and, by their growth, reveal its presence. As a ready means of discovering traces of phosphoric acid, this method will doubtless often commend itself to chemists; but I have considerable hopes that,

in a modified and extended form, it may be applied to the exploration of both air and water with far more valuable results. If the germ theory of disease be true, and it has of late received considerable experimental support, it is not improbable that the germ constituents of the air may undergo such a marked alteration during the prevalence of certain forms of epidemic disease, as to be recognisable in the growths which would ensue in such a fluid as that used in Experiment No. 9, or in a similar one to which some of the constituents of our ordinary food were added, such as albumin, milk, and juice of flesh. In order to expose these fluids with their contained germs to conditions as closely analogous as possible to those which obtain in the alimentary canal, they ought to be kept in the dark and maintained at blood-heat during incubation.

I have made a few experiments in this direction, but it is obvious that laborious and long-continued observations will be necessary before the ordinary developmental phenomena of a healthy atmosphere can be distinguished from those of infected air, and I will therefore only describe one or two of the experiments by way of illustrating the mode of operating. The process is also obviously equally applicable to the testing of waters intentionally infected by the evacuations of patients suffering from typhoid fever, cholera, scarlatina, and other diseases.

12. A sample of water supplied to London presented, three weeks after admixture with sugar and exposure to a temperature ranging between 60° and 70° F., faint traces of fungoïd growth. It was now placed in a nearly dark chamber at a temperature of from 78° to 85° F. After ten hours the development of mycelium had greatly increased, but on raising the temperature to 88°—99° F. for fourteen hours, the fungoïd threads nearly disappeared. Leptothrix fibres abounded, but no vibrios, bacteria, or moving organisms were seen.

13. Effluent water from Barking sewage farm was mixed with sugar and exposed, as in Experiment No. 12, to a temperature of from 78° to 85° F. for ten hours, at the end of which time it had become slightly turbid and a fungoïd growth was observed. The temperature was then increased to 98° F. Five hours later it had become very turbid and the fungoïd growth had augmented. After twenty-two hours' additional exposure to the same temperature the turbidity had considerably diminished and the fungoïd growth had not progressed much. The microscope revealed long, slender, fragile, and jointed mycelium threads, very different from those which had developed in similar liquids at more moderate temperatures. There were also crowds of bacteria, vibrios, and other moving organisms. Even at the expiration of a further period of three days, during which time a nearly uniform temperature of 98° F. was maintained, the fungoïd growth had not perceptibly increased.

14. Six drops of sewage and the usual proportion of sugar were added to about $1\frac{1}{2}$ oz. of Grand Junction Company's water, and the mixture, which smelt very offensively, was exposed as before to a temperature varying from 78° to 85° F. At the end of ten hours no perceptible change had taken place. The water was now raised to blood heat (98° F.), and maintained at that temperature until the close of the experiment. At the end of five hours it had become turbid from the development of crowds of bacteria. Even after the lapse of thirty hours more, no vibrios or mycelium were perceptible; but after the expiration of three more days, abundant fine long non-branching tubular threads, with square cells enclosed, had developed. Some vibrios and cells with bright nuclei were also seen.

From these and a number of other similar experiments, the conclusion was impressed upon me that the temperature of the body is favourable for the production of bacteria, vibrios, and similar organisms, but unfavourable for fungoïd growths. As already mentioned, however, these latter experiments will require to be greatly extended before any trustworthy conclusions can be drawn from them. It would be especially interesting to make them with water which had been agitated with the air of the fever, &c., wards of hospitals.

The following are the conclusions to which these experiments have led me:—

1. Potable waters mixed with sewage, urine, albumin, and certain other matters, or brought into contact with animal charcoal, subsequently develop fungoïd growths and other organisms, when small quantities of sugar are dissolved in them and they are exposed to a summer temperature.

2. The germs of these organisms are present in the atmosphere, and every water contains them after momentary contact with the air.

3. The development of these germs cannot take place without the presence of phosphoric acid, or a phosphate, or phosphorus in some form of combination. Water, however much contaminated, if free from phosphorus, does not produce them. A German philosopher has said, "*ohne Phosphor kein Gedanke.*" The above experiments warrant the alteration of this dictum to *ohne Phosphor gar kein Leben.*

Discussion.

President: It certainly is striking that the absence of phosphorus should cause the observed deficiency in the fungoïd development: but was phosphorus wholly absent? does not the sugar which is purified by means of animal charcoal contain some?

Prof. Frankland: The crystallisation of the sugar probably excludes any appreciable trace of phosphorus.

Mr. Heisch: In one or two points Dr. Frankland's observations are diametrically opposed to my own results. The one is that water cannot be deprived of its germs by filtration through animal charcoal. Now my observations in this respect are not isolated ones, but I have now for about three years been investigating week after week water which passed through charcoal filters, and have never met with fungoïd development in such water. The other point of difference between Dr. Frankland's experiments and my own is that, whereas he noticed the same kind of cells whether they were originated through white of egg or through sewage matter, I obtained in the two cases very distinct results. The sewage fungus is very small, perfectly spherical, and excessively transparent; it grows and decays rather rapidly; in about six hours after addition of the sewage fluid to the sugar solution the spherical cells, mostly in grape-like bunches, appear, which, after six more hours, have developed themselves into mycelia, and a few hours later are broken up entirely. During the growth of these organisms the odour of butyric acid was clearly perceptible. Now, when white of egg was put into a sugar-solution, no smell of butyric acid was emitted during the formation of the cells, which were somewhat larger and less transparent than those in the former case.

Dr. Russell: The results of my experiments mostly coincide with those arrived at by Mr. Heisch. I happened also to submit to the sugar-test a sample of drainage water from Romford Farm, and obtained, like Dr. Frankland, a negative result.

Mr. Bell: Perhaps the effluent water sample examined by Dr. Russell was kept for some time. In that case it would purify itself and give no fungoïd growth on addition of sugar. But if the samples of effluent waters are investigated very soon after they had been collected, they will yield fungi. Regarding Dr. Frankland's statements, I can say that my experiments fully bear out what he said with respect to the indispensable presence of phosphates. I can also fully confirm his remarks as to the animal charcoal—it does not take away the germs from the water; indeed I am inclined to believe that these germs live in the coal. I found burning to be the best means for purifying the charcoal.

Dr. Voelcker: Mr. Bell's remark as to the rapid change which sewage undergoes is quite correct. A jar of sewage left loosely covered for some months, had lost almost all its ammonia, whilst its nitric acid had increased. Since so much doubt is thrown on the efficiency of animal charcoal for purposes of water purification, I may mention that iron-sponge would be an excellent substitute for charcoal filters. This

spongy iron is obtained by calcining with coal the residues from copper pyrites.

Dr. Thudichum thought that the whole fungus theory was nothing better than a vague and wild surmise.

Mr. Warington: That water which had passed through iron-sponge does not yield fungi on addition of sugar may be due to the removal of the phosphoric acid which had been retained by the hydroxide of iron wherewith the sponge is covered. As to the experiments with charcoal I wish to observe that water filtering through fresh charcoal takes away from it some phosphates, but after the filter has been used for a time, this will no more be the case. This circumstance may perhaps explain the difference in the observations of Messrs. Frankland and Heisch.

Dr. Dupré asked whether Dr. Frankland and Mr. Heisch had boiled their sugar-solutions before mixing them with the waters to be examined? Whenever he (Dr. Dupré) did so, he obtained no fungi.

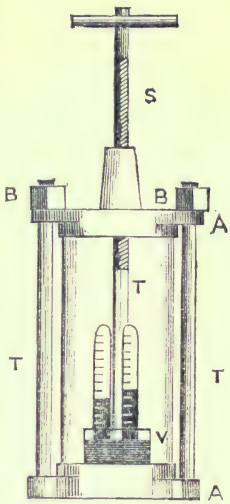
Dr. Frankland replying [to Dr. Dupré]: My sugar-solutions were not boiled, but in Experiment No. 9 the water had been previously boiled for a long time, and the sugar and all the other substances heated to a much higher degree than that of boiling water, and I obtained more splendid fungi here than in any other case. [To Mr. Heisch.] The difference in our observations regarding animal charcoal appears to be satisfactorily explained by Mr. Warington's observations. As to the two fungi, from sewage and from white of egg, I merely pronounced them to be similar to, but not identical with one another. I paid no particular attention to the emission of butyric smell. [To Mr. Bell.] I investigated the effluent water about 24 hours after its collection. (Here Dr. Russell remarked that he had done the same.) [To Dr. Voelcker.] I have also found that sewage is apt to have its ammonia converted into nitric acid.

IX.—*On the Effects of Pressure on the Absorption of Gases by Charcoal.*

By John Hunter, M.A., F.C.S., F.R.S.E., Professor of Mathematics and Natural Philosophy, University of King's College, Windsor, Nova Scotia.

In the following memoir, I purpose giving the results of a few observations on the effects of pressure on the quantity of a gas absorbed by cocoa-nut charcoal.

The form of apparatus employed in order to obtain pressure in these experiments, presents the great advantage of being easily taken to pieces, and when very high pressures are not required, I have found it to work admirably. Two strong copper plates (A A) are connected by means of three iron rods (T T T) firmly fastened to the lower, and passing through holes in the upper plate, where they are made secure by screws, and nuts (B). Each plate contains a groove in which is placed a leather washer, covered on the exposed surface with a mixture of white lead and grease. The ground ends of a thick glass cylinder are fitted against the leathers, and when the plates are screwed together, a strong joint is formed capable of resisting a pressure of about five or six atmospheres. The pressure is produced by first filling the glass cylinder quite full of water, and then introducing into it an iron screw (S), which works through leather packing.



In performing an experiment, a vessel (V) containing mercury is placed on the lower plate. Two tubes are inverted in the mercury; one partially filled with dry air, acts as a manometer; the other contains a fragment of charcoal and the gas under examination. The original volume of the gas is read off before introducing the charcoal into the tube, and after a sufficient time has elapsed, the amount of absorption is carefully determined. The glass cylinder is then placed over the tubes and the upper secured to the lower plate by means of the screws. The interior of the apparatus is now filled with water, and the pressure produced after the screw is measured by observing the volume of the air in the manometer tube. The corresponding diminution in the volume of the gas in the absorption tube is also read off, and since we know the original volume of the latter, we can easily calculate what it ought to be at each increase of pressure, and the difference between the observed and calculated volumes gives the absorption.

From the necessity of employing a comparatively small quantity of the gas in each experiment, rarely more than 5 or 6 c.c., the differences corresponding to each increase of pressure are not so regular as I could have wished; nevertheless, in comparing the results contained in the following tables it may be observed, first: that the amount of absorption increases with the pressure to which the gas is exposed; and, secondly, the same change of pressure produces about the same amount of increase in the quantity of each gas absorbed.

It is worthy of observation that if we compare the relative *weights*

of the absorbed gases in the following tables, we find that cocoa-nut charcoal absorbs a greater weight of cyanogen than of either ammonia or carbonic anhydride.

In the tables of absorptions :—

V = the volume of gas absorbed by one volume of cocoa-nut charcoal at 0° C. and the corresponding pressure.

P = the pressure in millemetres to which the gas is exposed.

Ammonia.

First Series.		Second Series.		Third Series.	
V.	P.	V.	P.	V.	P.
170·4	760·0	170·7	760·0	165·5	760·0
173·0	1102·0	174·3	1104·3	166·4	850·7
176·9	1170·4	176·0	1178·0	173·0	1380·2
178·2	1367·2	178·2	1269·2	176·9	1639·8
179·5	1479·7	180·8	1369·5		
		183·5	1486·5		
		188·7	1795·1		
		196·7	2002·6		
		209·8	2608·5		

Fourth Series.		Fifth Series.		Sixth Series.	
V.	P.	V.	P.	V.	P.
170·6	760·0	174·2	760·0	172·7	760·0
171·7	1013·8	177·0	1278·4	178·2	828·5
173·0	1095·9	182·2	2407·9	180·8	950·2
176·9	1149·1			183·5	1024·9
				184·8	1112·9
				187·3	1217·3
				190·0	1343·5
				194·0	1498·7
				197·5	1693·9
				201·9	1955·9

Carbonic Anhydride.

First Series.		Second Series.		Third Series.	
V.	P.	V.	P.	V.	P.
78·2	760·0	61·7	760·0	71·1	760·0
91·1	1009·3	84·5	1480·7	76·9	892·4
91·7	1073·8	86·0	1688·1	77·4	962·9
93·1	1333·6	87·7	2397·0	77·9	1045·6
96·6	1450·5	95·0	2910·8	78·4	1143·7
		102·1	3858·2	80·0	1262·2
				81·1	1408·0
				82·5	1594·5
				88·6	2143·4

Carbonic Anhydride—continued.

Fourth Series.		Fifth Series.	
V.	P.	V.	P.
69·7	760·0	73·2	760·0
79·5	938·6	84·0	927·9
80·5	1035·6	85·5	1014·6
81·5	1155·9	87·3	1100·2
82·0	1306·4	91·6	1412·8
84·5	1503·3	95·5	1625·6
85·8	1778·4	100·4	1912·9
86·1	2190·3	108·0	2324·1
		113·0	2960·2
		132·4	3793·2

Cyanogen.

First Series.		Second Series.		Third Series.	
V.	P.	V.	P.	V.	P.
103·5	760·0	106·7	760·0	106·6	760·0
106·8	960·8	107·7	1146·8	114·1	1011·2
107·7	1051·1	108·5	1510·6	115·0	1143·3
109·9	1159·9	109·0	1886·3	117·1	1315·1
112·8	1293·5	109·9	2403·1	118·4	1880·2
114·5	1463·0				
116·3	1681·9				
129·2	1980·5				

Fourth Series.		Fifth Series.		Sixth Series.	
V.	P.	V.	P.	V.	P.
103·2	760·0	107·5	760·0	102·5	760·0
105·1	1031·3	107·7	1169·6	103·4	1212·3
106·8	1101·2	110·3	1291·2	104·7	1338·4
108·5	1182·5	112·0	1628·8	106·4	1493·4
110·3	1276·0	115·4	1873·4	112·0	1942·5
111·3	1335·5	121·0	2204·7	119·3	2286·8
112·2	1515·4	124·9	2678·2		
113·3	1865·8				

X.—*On the Solubility of the Phosphates of Bone-Ash in Carbonic Water.*

By Robert Warington.

In the year 1866 I brought before the Society some results of an investigation into the solubility of tricalcic phosphate under various conditions which might be supposed to occur in soil.* The results described in that paper were obtained with pure salts artificially prepared. It was intended, in the next place, to examine the various natural mixtures which form the phosphates available for agriculture, and to ascertain their solubility under similar conditions. The investigation of this second part of the subject was commenced at the Royal Agricultural College during the spring of 1867, but was soon afterwards unavoidably relinquished. Having no prospect of completing the experiments, I desire to put on record the results then obtained.

Two specimens of bone-ash were the phosphates examined—one, a commercial sample of unknown history and fair average quality, the other a sample of pure bone-ash from Rothamsted, kindly furnished by Mr. Lawes, representing the carcass bones of an entire ox. These specimens of bone-ash were analysed, with the following results:—

	Commercial Bone-ash.	Pure Ox Bone-ash.
Moisture and volatile matter	6·70	1·86
Siliceous matter	9·69	·51
Oxide of iron	·58	·17
Lime	43·37	52·46
Magnesia	1·14	1·02
Phosphoric acid	33·68	39·55
Carbonic acid, alkalies, and other substances undetermined	4·84	4·43
	100·00	100·00

A preliminary experiment was made with the commercial bone-ash. An unknown quantity† was treated with water, and carbonic acid passed into the mixture, the end of the delivery-tube being so placed that the passage of the gas kept the bone-ash in suspension. After five days the solution was removed and analysed. The results were most unexpected. Ten thousand parts of the solution contained 2·495 P_2O_5, a degree of solubility equal to that of gelatinous tricalcic phosphate in carbonic water. A large quantity of magnesia was also

* Jour. Chem. Soc., 1866, vol. iv, p. 296.

† In this case the bone-ash was well washed with hot water before the experiment commenced. This was not done in the subsequent experiments.

present, more than sufficient to convert all the phosphoric acid into pyrophosphate.

From this first trial it appeared very probable that a part of the phosphoric acid in bone-ash existed in a comparatively soluble form, since it was most unlikely that the high degree of solubility just mentioned would be sustained during successive treatments with carbonic water. In order, therefore, to ascertain the *permanent* solubility of the phosphates of bone-ash, 400 grains of the commercial bone-ash were placed in a pint bottle, and subjected to repeated treatment with water and carbonic acid, each solution of bone-ash being removed by decantation, and analysed, while the residue was subjected afresh to the process of solution, the intention being to continue this mode of proceeding until the amount of phosphoric acid removed ceased to vary. A similar series of solutions was made with the pure bone-ash; but it having been found that the solubility decreased very slowly in the earlier series of experiments, only 300 grains of this bone-ash were operated on. In every case the carbonic water remained in contact for three or more days, during which gas was passed for 16 to 24 hours. The results obtained are shown in the following tables:—

I. *Experiments on the Solubility of Commercial Bone-ash.*

Number of solution.	Found in 10,000 parts of each solution.															Total dissolved for 100 originally present in the Bone-ash.
	I.	II.	III.	IV.	V.	VI.	VII.	VIII	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	
P_2O_5	2·353	1·473	1·159	1·073	1·000	·970	1·288	1·173	1·110	1·026	·909	Not	·779	·831*	·758	11·35†
CaO.....	1·918	2·226	1·747	1·547	1·419	1·279	1·789	1·572	1·433	1·329	1·163	ana-	1·009	...	·951	11·34†
MgO	1·595	·572	221	·118	·070	·079	·191	·073	·066	·070	·053	lyzed	·040	...	...	65·79†

II. *Experiments on the Solubility of Pure Ox Bone-ash.*

Number of solution.	Found in 10,000 parts of each solution.								Total dissolved for 100 originally present in the Bone-ash.
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	
P_2O_5	1·010	·634	·538	·581	·669	·662	·674	·696*	4·19
CaO.....	1·376	1·188	·943	·919	·956	·892	·874	..	4·63†
MgO	2·382	·526	·125	·063	·056	·045	·031	..	96·34†

* Determined with uranium.

† Where determinations were wanting, an estimate has been introduced in calculating this number.

Between experiments VI and VII with commercial bone-ash, and between experiments IV and V with pure bone-ash, the undissolved phosphates were removed from the bottle and reduced to the finest powder obtainable.

In the first series of experiments there is a gradual decline in the amount of phosphoric acid dissolved, and the figures give no evidence that the minimum solubility was reached even at the end of the series. The amount of phosphoric acid taken up by the first solution is about three times as great as that dissolved by the fifteenth treatment with carbonic water. The real difference between the primary and final solubility of the bone-ash phosphates was probably however far greater than this. For since it is shown by the experiments that only a small fraction of the phosphates possessed a high degree of solubility, it is clear that to obtain a saturated solution of these phosphates it was necessary that the quantity of bone-ash should bear a high relation to the volume of solvent, which in fact it did not.

The magnesium salts in the bone-ash appear to be much more soluble than the calcium salts, as indeed was to be expected from previous researches. The large amount of magnesia taken up by the first solution is however very remarkable.

The last column in the table shows that the carbonic water had, on the whole, removed phosphoric acid and lime in the same proportions as they existed in the bone-ash; and that about two-thirds of the magnesia had been dissolved for one-ninth of the phosphoric acid and lime.

In the series of experiments with pure ox bone-ash, it is at once evident that the phosphate was of a much more uniform composition than the commercial bone-ash used in the preceding trials. The amount of phosphoric acid taken up soon fell to a minimum, and remained very constant to the end of the experiment, though the amounts of lime and magnesia removed continued to diminish.

Taking the mean of the last four trials as representing the permanent solubility of the phosphates of this bone-ash, we have a solubility of ·675 P_2O_5 in 10,000 of carbonic water.* Or, reckoning the phosphoric acid as tricalcic phosphate, for the sake of comparison with other results, the solubility is 1 of phosphate of calcium in 6788 of carbonic water.

The table shows that the primary solubility of the phosphates was much less in the case of the pure bone-ash than in the case of the commercial sample. The difference is doubtless in part owing to the smaller quantity of the pure bone-ash operated upon, the bulk of fluid

* It will be observed that the permanent solubility here obtained is quite near to the last solubility in the preceding series. It seems probable, therefore, that the minimum solubility had been almost reached in the first series of experiments.

remaining the same in both cases. This fact, however, can explain but a small part of the difference, which must be mainly due to the more uniform character of the pure bone-ash. On comparing the analyses of the two bone-ashes already quoted, the only marked difference which appears is the far larger amount of siliceous matter in the commercial sample. It seems likely that in the process of calcination the sand had to some extent attacked the phosphate of calcium, producing silicate of calcium, and leaving phosphates less basic than those constituting normal bone-ash. If this be the case, the greater primary solubility of the phosphates in the commercial bone-ash was owing to the presence of a small portion of comparatively acid phosphates.

The high solubility of the magnesium salts is even more strikingly shown with the pure bone-ash than in the previous results.

The whole effect produced by the carbonic water upon the pure bone-ash is shown by the table to have consisted in the removal of but a small quantity of the phosphoric acid and lime (the latter dissolved in somewhat larger proportion than the former), while nearly the whole of the magnesia was taken up.

It is not supposed that the results of these detached experiments are of much importance to the agricultural chemist; it is, indeed, only from a comparison of the behaviour of different phosphatic materials that any valuable conclusions are to be expected. The results show however, unmistakably, the vast difference which may exist between the primary and permanent solubility of a complex body, and point to the necessity of operating by the method of successive solutions whenever the permanent solubility is to be ascertained. This method, as far as I am aware, has been scarcely used, and the solubilities of natural phosphates and other bodies have been thought to be sufficiently determined by single or independent experiments. This plan, which is all that is required with pure salts, is quite inadmissible with complex bodies, and must frequently lead to very erroneous conclusions.

Dr. Voelcker observed that the circumstance that at first greater quantities of phosphoric acid went into solution might be due to the presence of alkalis. Moreover, commercial bone-ash is prepared, not from pure bones, but from such as have been mixed with dried blood, &c., which of course would explain the greater amount of soluble phosphates.

Mr. Gill remarked that in the analyses of commercial bone-ash—so called bone-saw-dust—he had mostly found the alkalis in the state of chlorides.

Mr. Warington confirmed this statement.

XI.—*On the Distillation and Boiling Point of Glycerin.*

By Thomas Bolas.

It is well known that when glycerin, subjected to the ordinary atmospheric pressure, is heated so much as to cause ebullition, it is more or less rapidly decomposed; and that almost the whole of the glycerin operated on may be decomposed by repeated distillation. This decomposition may, however, be entirely prevented by a reduction of the pressure in the apparatus employed to 12—50 mm.

The boiling-point of glycerin was determined by effecting the distillation in a long-necked flask, having a supplementary neck attached at right angles to the principal one. In the principal neck the thermometer was fixed by the aid of a caoutchouc cork, while the smaller neck was connected in a similar manner with a two-necked receiver. The glycerin, together with a few fragments of tobacco-pipe (this latter being required to prevent the bumping which would otherwise occur), being placed in the retort-flask, the receiver was connected with a Sprengel's mercurial pump and a manometer, the caoutchouc joints being made air-tight with glycerin in the usual way. Unless the glycerin distilled had been dehydrated by previous distillation in a vacuum, the first portion of the distillate consisted principally of water; afterwards, when the glycerin in a pure state came over, the temperature indicated by the thermometer was 179·5° C. At this time the pressure on the liquid was 12·5 mm., a pressure nearly corresponding to the tension of aqueous vapour at the temperature of the receiver.

A determination of the carbon and hydrogen in the glycerin distilled as above, was made, the oxidant employed being copper oxide, followed by oxygen gas.

I. ·4281 grm. substance gave ·6102 grm. CO_2 and ·3439 grm. H_2O.

	Theory.		Found.
			I.
C_3	36	39·1	38·9
H_8	8	8·7	8·9
O_3	48	52·2	—
	92	100·0	

Under a pressure of 50 mm., glycerin distils, without change, at about 210° C.

Glycerin dehydrated by distillation absorbs water from the atmosphere to the extent of about 50 per cent. of its weight. The amount absorbed is, as might be expected, very variable.

XII.—*On the Action of Heat on Silver Nitrite.*

By Edward Divers, M.D.

The Handbooks give us no information on this subject. Péligot is, I believe, the only chemist who has written anything about it. In his well-known memoir on Hyponitric and Nitrous Acids,* he states that he tried to prepare nitrous anhydride by distilling silver nitrite, and that he obtained instead nitrosonitric anhydride, the nitrite being converted into nitrate by the first portions of the anhydride disengaged by the heat. Having need, for the purposes of another investigation, to be familiar with the action of heat on this salt, I examined it with the results now to be described.

The products of this action consist principally of silver nitrate, reguline silver, and oxides of nitrogen. But the relative proportions of the quantities of these substances to each other, and, as a consequence of this, the composition also of the gaseous matter, vary considerably in different experiments.

When silver nitrite is heated in a crucible or watch-glass over a lamp, its decomposition becomes first evident by its turning grey where in contact with the hot crucible, and by its giving off red fumes. The mass very soon enters into a state of semi-fusion and intumescence, and then becomes solid again and of a whitish-grey in some parts and greenish-yellow in others, red fumes still being produced, but much less copiously than during the intumescence. Lastly, on continuing the heat, the yellow portions of the mass slowly change to grey like the rest, with formation of a small quantity more of red fumes. Prolongation of the heat beyond this point causes the glass or porcelain to be attacked; but as the entire greying of the mass has been found to be a sign that nothing, or almost nothing, remains but silver nitrate and free silver, it is here unnecessary to pursue beyond this point the changes which take place.

As there is found to be a material difference in the loss of weight sustained in different experiments, it might naturally be supposed at first that this is due to a decomposition of the silver nitrate formed; but that it is not so, is shown, firstly, by the fact that longer heating at about the same temperature causes very little more loss; secondly, that the temperature does not appear to be so high as that required for the free decomposition of silver nitrate; and, thirdly, that the loss sustained bears no direct relation to the degree of heat employed.

* Sur l'acide hypoazotique et sur l'acide azoteux. Ann. de Chimie et de Phys. [3], vol. ii (1841), p. 58.

When the nitrite in an open dish is heated in an oven at any temperature between about 85° on the one side and 140° C. on the other, it loses its sensible characters almost imperceptibly, becoming whitish-grey and non-crystalline, without fusion or any apparent change in bulk.

The change which takes place in the nitrite, when it is heated in an open vessel in either of the above ways, does not generally differ very much in its results from that represented by the equation—

$$3NO_2Ag = N_2O_3 + Ag_2 + NO_3Ag.$$

as the following experiments show:—

I. 1·005 grm. was moderately heated over the lamp in a crucible, so as to effect rapid decomposition. When this seemed complete, the lamp was removed. During the heating, a little metallic fume escaped along with the oxides of nitrogen. The lid of the crucible was raised once or twice during the heating, and again afterwards, and the red fumes allowed to disperse. The contents of the crucible were washed with water and the residue dried, weighed, and proved to be reguline silver by its losing only three-tenths of a milligramme on ignition. Before washing out, the residue weighed ·849 grm., and after washing out and ignition, ·426 grm. By deducting the reguline silver obtained from the total silver in the original salt, the soluble matter was shown to have contained a little unchanged nitrite. The ratio of the reguline silver to the volatile matter is nearly that of $Ag_2 : N_2O_3$.

II. 1·219 grm. of the nitrite was heated in an open watch-glass over the lamp till all the yellow portions of the mass had just become grey. The mass was weighed, washed out with water, dried and weighed again. It was then ignited, and found to have lost only half a milligramme by the operation. There was material loss by the considerable spirting and throwing off of metallic fume which occurred during the intumescence, and, therefore, the silver in the matter afterwards dissolved out by water, was determined as chloride. The soluble matter contained a very little nitrite, as was shown by its action on potassium permanganate, imperfectly estimated by this reagent to be about ·01 grm.

Before washing out, the residue weighed 1·012 grm., and after washing out and ignition, ·528 grm. The matter dissolved out by water gave ·408 grm. silver chloride = ·307 grm. silver. Deducting the total silver found in the residue after the application of heat from that in the nitrite used, the amount of loss by spirting, &c., was determined, and found = ·027 grm. nitrite. In calculating the percentage relations of the products of the decomposition, this quantity, therefore, of nitrite was deducted from the quantity taken for the ex-

periment, and also from the loss caused by heat. The ratio of the reguline silver to the volatile matter is nearly that of $Ag_2 : N_2O_3$.

In another experiment, just like the last, the gross loss by heat was in the same proportion to the nitrite used as in the last experiment. This experiment was not pursued further.

III. ·535 grm. of nitrite was heated in an oven for nearly forty hours at a temperature of about 98°, and was found, by repeated weighings, to be losing weight during all this time. It was then maintained for twelve hours longer at a temperature of 110°—125°, and lost only ·0002 grm. more. The loss by heat = ·080 grm. What was left was washed out with water, dried, and reweighed. The residue was not ignited, but other experiments to be described prove that it was metallic silver. It weighed ·237 grm. The ratio of this residual silver to the loss sustained by heat is closely that of $Ag_2 : N_2O_3$.

The silver nitrite employed for these experiments and the others recorded in this paper, was carefully prepared, and some of it ascertained to contain 70·06 per cent. silver, estimated as chloride. The theoretical quantity is 70·13.

The percentage numbers for the preceding experiments, and those for the equation to which they are referred, are these :—

	Calc.	I.	II.	III.
Volatile	16·45	15·5	15·1	15·0
Reguline silver	46·75	42·4	44·3	44·2
Soluble	36·80	42·1	40·6	40·8
	100·00			

When, instead of employing an open crucible or dish for heating the nitrite over the lamp, a closely-covered one is used, so that the gaseous and fixed products of decomposition may be kept for a time in contact, the loss of weight experienced by the mass is less and the amount of nitrate formed is greater.

The ultimate change effected in this way approaches, though not closely, to that expressed by the equation—

$$2NO_2Ag = NO + Ag + NO_3Ag.$$

The following experiments are adduced in support of this statement :—

IV. ·301 grm. was heated in a watch-glass covered by another. It gave ·040 grm. gases, and ·261 grm. metallic silver, the rest being soluble. The ratio of the metallic silver to the gaseous matter is about the mean of those of $Ag : NO$ and $Ag_2 : N_2O_3$.

V. ·768 grm. was heated in the same way, but not quite so fully, as

in the last experiment. It gave ·077 grm. gases, and ·265 grm. metallic silver, the rest being soluble and found to contain some nitrite. The ratio of the silver to the gaseous matter is nearly that of Ag : NO.

VI. 1·022 grm. was heated till the watch-glass began to be acted on by the nitrate produced. The gases expelled = ·118 grm. and the metallic silver left = ·379 grm. The ratio of the silver to the gaseous matter approaches that of Ag : NO.

VII. 1·218 grm. was heated in a covered watch-glass, immediately after the heating of the same weight of nitrite in an open watch-glass, in the experiment marked II, over the same gas flame, and at the same height from it; so that this experiment and Experiment II, are parallel ones, and serve to show strikingly the effects of covering the nitrite during heating. The process was also carried just to the same point, as regarded the appearance of the mass. The only difference was, that the glass being covered, less heat was lost by radiation, and the change was therefore sooner completed. As in the other case, the soluble matter contained a very little nitrite. The loss by heat, including a little metallic fume, = ·151 grm., and the weight of the metallic silver = ·468 grm. The ratio of the silver to the gaseous matter is nearly the mean of Ag : NO and $Ag_2 : N_2O_3$.

For the sake of comparison, the percentage numbers of these experiments and those calculated for the equation to which they are referred, are added—

	Calc.	IV.	V.	VI.	VII.
Volatile	9·74	13·3	10·0	11·6	12·4
Reguline silver ..	35·06	41·5	34·6	37·1	38·4
Soluble	55·19	45·2	55·4	51·3	49·2
	100·00				

The indication of these numbers is rendered more evident by comparing them with those of the first table. But more conclusive evidence can be brought forward that the effect of keeping the gases given off in contact with the undecomposed nitrite remaining is to cause nitric oxide alone to be lost. This has been obtained by so heating the nitrite in a vessel nearly closed, as to decompose it only very gradually.

VIII. ·4433 grm. of the nitrite was placed in a small tube, and the empty portion of the tube filled up by a glass rod barely small enough to be pushed into it. After 12 hours, at about 90°, it weighed ·4431 grm.; after 12 hours more, at 95°–99°, it weighed ·4437 grm.; after 12 hours more, at 115°—135°, ·446 grm.; after 14 hours more, at about 134°, it weighed ·450° grm.; after again 14 hours, mostly at 136°, ·453 grm.; and after 14 hours more, when the heating was discontinued, ·4544 grm. There was, therefore, instead of a loss, a material gain in

weight = ·0111 grm. Faintly reddish gas was first detected in the tube at 115°. At 134° the crystals began to shrink and fuse together, and this occurred first near the stopper of the tube, and only very slowly proceeded backwards to the end of the tube. It would not therefore be right to conclude that silver nitrite fuses at this temperature, the fusion apparently taking place only in the nitrite after it had become mixed with nitrate. During the heating the mass scarcely altered in colour. The explanation of the gain in weight is, of course, evident. The nitrite decomposing and evolving nitric peroxide, or at any rate a nitrogen oxide, this becomes reduced to nitric oxide, if not already such, by oxidizing unchanged nitrite; the nitric oxide then serves as a carrier of atmospheric oxygen to the nitrite, as it is known to do to other substances. The extent to which atmospheric oxygen was thus fixed in the preceding experiment is more fully shown by the examination which was made of the contents of the tube. These were treated with water, and found to contain ·0216 grm. of metallic silver, which, therefore, as nitrite, had been in combination with ·0092 grm. gaseous matter. This loss being balanced against the oxygen absorbed, its weight must evidently be added to the observed gain in weight, to obtain the actual amount of oxygen absorbed by the rest of the nitrite. The total oxygen absorbed is therefore equal to ·0203 grm. Of this, about ·017 grm. must have been derived from the air, the rest coming from the decomposed nitrite, thus:—

$$NO_2Ag = Ag + NO + O.$$

I have calculated that not very much less than half the nitrite was converted into nitrate in this experiment.

This experiment is sufficient to establish that hot nitrite reduces the higher oxides of nitrogen to nitric oxide, so that we have proof that the tendency under one set of circumstances is to convert nitrite into the ultimate products, metallic silver, nitric oxide, and silver nitrate, according to the equation already given. But it is quite clear that nitric oxide and the silver nitrate are secondary products of the action of heat. This can, however, be shown, in another way, to be undoubtedly the case, as in the following experiments.

IX. 2·098 grms. were heated in a dish in an oven for 72 hours, at a temperature of about 98°, in a moist atmosphere, obtained by keeping a dish of water in the oven. The loss in this experiment = ·441 grm., and the residual mass, by washing out with water and re-ignition, yielded 1·157 grm. of silver. The soluble matter contained a little nitrite.

X. ·794 grm. was heated for about 95 hours in an atmosphere of steam, at a temperature rising from 98° to 140°. The residue weighed ·580 grm. This experiment was not pursued furth.er These two

experiments are sufficient to establish the fact that, under a given set of conditions, namely, free exposure in a moist atmosphere, silver nitrite tends to yield only metallic silver and nitrogen peroxide, thus :—

$$NO_2Ag = Ag + NO_2,$$

as the percentage numbers of the above experiments and those for this equation will show, when compared with those already given :—

	Calc.	I.	II.
Volatile.....	29·87	21·4	27·0
Fixed.....	70·13	—	—
	100·00		

The conclusion, then, from all these experiments is that, like other silver salts, the nitrite splits up, under the influence of heat, into metallic silver and the acid radical or its components, and that silver nitrate, nitric oxide, and perhaps nitrous anhydride, are formed only by secondary reactions. With regard to nitrous anhydride, the experiments which have been here given to prove that the gases evolved are either nitrous anhydride or its equivalent, furnish no proof that they actually include this body.

On decomposing the nitrite by heat over the lamp until fusion and intumescence have just ceased, the mass is of a greenish-yellow, as I have already mentioned. If the mass be then washed with water, it will be found that though much of this coloured matter consists of, or contains nitrite, the colour of the mass is partly due to a small quantity of bright-yellow matter that is left after thorough washing along with the silver. This matter is unaffected by light, soluble in ammonia, insoluble in water, and decomposed by boiling in water. I have not examined it, but its probable composition is I think, indicated by some experiments of quite a different character from the present, an account of which, however, I am obliged to reserve for another paper, about to be published, on an essentially different subject.

The fusion which occurs in the mass of heated nitrite so soon as it has undergone some oxidation, suggests that the nitrate formed combines with the nitrite to form a nitrite-nitrate, or hyponitrate. The point at which this fusion occurs is far below that at which silver nitrate fuses. In Experiment VIII the nitrate formed is calculated to have been in nearly the proportion of one atom to one atom of the undecomposed nitrite. It is, therefore, not improbable that an unstable nitrito-nitrate exists.

The President inquired in what way Dr. Divers had ascertained that the solid residue contained no argentic oxide ?

Dr. Divers replied that the washed residue had the appearance of metallic silver, and that after weighing it he had subjected it to strong ignition and then weighed it again; there was only a difference of a few tenths of a mgm. between the two weighings.

Dr. Odling asked what the evidences were for assuming the existence of a silver nitrito-nitrate? The existence of such a compound would necessitate a modification of the views at present entertained on the constitution of salts.

Dr. Divers said that his supposition rests on the circumstance that the nitrite began to fuse at about 134° after partial decomposition. Since the melting point of silver nitrate is much above that degree, he attributes it to a compound of the nitrite and the nitrate, having, like some alloys, a lower melting point than either of its components. But, on the whole, he considers the combination only a loose one.

Dr. Odling observed that the circumstance which Dr. Divers had mentioned was only an instance of what occurred in some other cases of mixture of two salts, for it is well known that such mixtures fuse at some lower degree of temperature than either of the salts separately.

Dr. Divers agreed with Dr. Odling that the evidence for the existence of a nitrito-nitrate is but a slender one. In Experiment VIII, however, when complete fusion of the mass had taken place, the proportion of the nitrate formed to that of the nitrite left undecomposed was that of one atom to one atom. He himself, however, found it hard to admit the existence of a silver hyponitrate, silver being univalent. It stood differently with lead, which is a bivalent metal.

Dr. Armstrong remarked, in support of the existence of the new salt, that Prof. Wislicenus had, in a recent publication, stated some reasons for viewing silver as a bivalent element.

Dr. Mills asked what proof there was that the gas evolved in some of the experiments really was nitrous acid, and not a mixture of nitric oxide and oxygen?

Dr. Divers did not intend to insist upon the former view; he quite admitted the possibility of the gas being such a mixture, or one of nitric oxide and nitric peroxide.

XIII.—*Laboratory Notes on the Examination of Glucose-containing Sugars.*

By C. Haughton Gill.

Those engaged in the examination of low sugars and molasses, have frequently had to complain of obtaining quite unintelligible results. It

is well known that the solution of the sugary body is decolorised, and clarified by the addition of basic lead acetate, before submitting it to optical examination—but I find that the power of invert sugar to rotate a ray of polarised light, is so greatly altered by the presence of this reagent, that the results obtained by the so-called polarisation of syrups containing much invert sugar, are worthless when clarification has been effected in the ordinary way.

The alteration of rotatory power of pure invert sugar by basic lead acetate, is shown by the following experiments:—

15 c.c. of a solution of invert sugar made up to 50 c.c. by water	Observed with a Soleil's saccharometer* in tube of 20 c.m.	read − 28·25 at 24° C.
15 c.c. of the same solution, with water, and 2 c.c. of saturated solution of basic lead acetate to 50 c.c.	.. .. ..	„ − 24·7 at 24° C.
15 c.c. of the same solution with basic acetate solution alone to 50 c.c.	.. .. ..	„ + 57 at 25° C.

These results have been confirmed by many other observations.

The alteration producing this reversal of rotatory power, takes place only on the *levulose* of the liquid—the *dextrose* suffers no change of optical properties.

A solution of pure *dextrose* prepared from invert sugar, and reading 60·3, made up to 2 vols. by strong solution of basic lead acetate.	read 30·5.
A solution of nearly pure levulose, prepared by Dubrunfant's method, and reading − 44 at 20° C., made up to 2 vols. by solution of basic lead acetate.	„ + 6 at 20° C.

The maximum alteration of rotatory power caused in this way, seems to be equal to that which would be caused by converting all the levulose into an equal weight of dextrose.

This reaction also affords a means of detecting the levulose in presence of an excess of dextrose.

The alteration of the rotatory power of levulose is not permanent. On removal of the lead or on acidifying the liquid, the original rotatory power is restored. The alteration is not due to the alkalinity of the lead solution, as regards alkalinity alone, for weak soda, or ammonia produces no such change, till it begins to decompose and destroy the sugar. It is probable that a soluble lead compound of levulose possessed of dextro-rotatory power is formed.

Now, when a sugar solution containing invert sugar is clarified by basic lead acetate, the invert sugar loses, in part or in whole, its levorotatory power, and the first direct reading is too high. When the liquid

* The readings of this instrument $\times \frac{25 \cdot 8}{100}$ = angular degrees.

is acidified and inverted by heat, the original invert sugar has its true levorotatory power restored, and added to that of the invert sugar proceeding from the cane-sugar, thus producing a greater "difference" in the readings than that due to the cane-sugar alone, and consequently leading to too high a result.

The remedy for this difficulty is to remove the lead, and acidify the liquid before making the first reading. For this purpose, I prefer to use a strong solution of sulphur dioxide, which possesses the advantages of removing the lead, and bleaching the liquid at the same time, while it is incapable of inverting cane-sugar in the cold, even in twenty-four hours. The decolorising effect is so great, that even the worst treacles give liquids of a pale straw colour when thus treated, and moreover, "inversion" can afterwards be performed without any fear of spoiling the colour; whereas, by the ordinary method, the liquid frequently becomes too red to allow of optical examination.

Another error also arises from the use of the lead-salt as a clarifier for those sugar solutions in which glucose is to be estimated by the use of Fehling's copper solution. The presence of lead here leads to a result much too low since it also becomes partly reduced, and thereby necessitates the use of a greater volume of the saccharine solution, which is called on to reduce lead, as well as the known amount of copper. Sulphur dioxide serves to remove the lead, while excess of the reagent exerts no other action on the copper solution, than that of facilitating the subsidence of the cuprous oxide.

As illustrating the extent of the error which may be introduced by the presence of lead, the following experiment, selected from many others, may be taken.

Solutions of invert sugar of the same strength used in each case.

	Volume required to precipitate cuprous oxide from 10 c.c. of Fehling's liquid.
1. Free from foreign bodies	10 c.c.
2. Containing 10 per cent. of its volume of solution of basic lead acetate.....	17 c.c.

To utilize these observations, the practical course of analysis of a low sugar or molasses, becomes

Weigh off double normal quantity; dissolve, treat with excess of basic acetate, and make up to 100 c.c.; filter; measure off 50 c.c. of filtrate; make up to 100 c.c., by solution of sulphuric dioxide; and filter again. This solution will have the usual degree of concentration, and can be proceeded with, as if prepared in the ordinary manner from good sugar.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

Researches on the Specific Heats, Densities, and Expansions of some Liquids. By C. MARIGNAC.*

PART I.—SPECIFIC HEATS. The specific heat of aqueous solutions is estimated as follows. A large sized mercurial thermometer, with a spirally coiled tube for a reservoir, is heated in an oven to a few degrees above the point required. On being taken out, it is brought near to the calorimeter, in which it is immersed the instant the mercury in the stem has fallen to the desired point. The calorimeter contains the liquid, the specific heat of which is to be estimated, and the quantity of liquid employed is regulated so that the introduction of the heated thermometer produces in every experiment sensibly the same elevation of temperature. Under like atmospheric conditions all exterior disturbing causes thus influence the temperature of the calorimeter to the same extent in every experiment, and have no influence on the result. All corrections may therefore be dispensed with. To ensure these like conditions the experiments performed on each solution are made to alternate with the parallel experiments on water, and are thus strictly comparable with these latter. The quantities of liquids used are inversely proportional to their specific heats. For saline solutions a silvered brass calorimeter is employed; for strongly acid liquids a thin glass vessel is substituted.

The specific heat of more volatile liquids is estimated by enclosing them in a thin glass bulb containing a small, but sensitive thermometer, and employing this bulb, instead of the large mercurial thermometer, as the source of heat. In these cases the calorimeter, of course, always contains the same amount of water, and the quantity of liquid used in the bulb is so adjusted that it has always the same capacity for heat, and therefore produces the same elevation in the temperature of the calorimeter. The experiments, as in the previous case, being comparative, all corrections for loss by radiation, &c., are here also dispensed with. Different experiments, made by the foregoing methods, with one and the same liquid, give extremely concordant results.

In what follows C stands for the molecular heat of the various liquids employed, n for the number of molecules of water to one molecule of the substance dissolved.

Sulphuric acid, $H_2O.,SO_3 + n$Aq.—The acid employed had been purified by distillation, and brought to the monohydrate by repeated

* Phil. Mag. [4], xli, 134.

congelation. Experiments made by the first method lead to the following empirical formula for the calculation of C :—

$$C = 18n + 8{\cdot}58 + \frac{334{\cdot}8}{n} - \frac{2882}{n^2} + \frac{7262}{n^3}.$$

The formula is inapplicable to solutions containing less than 5 molecules of water. The specific heat of the monohydrate was found to be 0·3315 for temperatures between 16° and 20°. Some experiments made by the second method, on mixtures with less than 5 molecules of water, gave the following results for the specific heat between 20° and 56° :—

	Specific heat.	Molecular heat.
Monohydrate	0·3363	33
With 1 molecule of water	0·4411	51·2
„ 3 „ „	0·5056	76·8
„ 5 „ „	0·5833	109·7

These results agree well with those of the first series, and also confirm the curious fact established by Pfaundler, that the first equivalent of water added to monohydrated sulphuric acid increases the molecular heat by a quantity precisely equal to that of the water added, while for every further dilution there is a considerable loss of molecular heat.

Sodium sulphate, $Na_2O.SO_3 + n$ Aq.—Experiments on solutions with 50, 100, and 200 molecules of water respectively, lead to the following formula for C :

$$C = 18n - 16{\cdot}34 + \frac{4094}{n} - \frac{98000}{n^2}.$$

The formula becomes inaccurate in the case of weaker solutions. For solutions containing more than 200 molecules of water the specific heat is less than that of the water alone; the specific heat is always diminished by the addition of water.

Sodium-hydrogen sulphate, $\left.\begin{matrix}Na\\H\end{matrix}\right\} O.SO_3 + n$ Aq.—The empirical formula for C is

$$C = 18n + 11{\cdot}65 + \frac{1292}{n} - \frac{11500}{n^2}.$$

A comparison of the molecular heats of solutions of sulphate of sodium, bisulphate, and of sulphuric acid of corresponding strengths, shows that the molecular heat of bisulphate solutions is always above the mean of the molecular heats of the neutral sulphate and of sulphuric acid. The mixing of these two substances produces a lowering of temperature.

Hydrochloric acid, $HCl + n$ Aq.—In this case, $C = 18n - 28{\cdot}39 + \frac{140}{n} - \frac{268}{n^2}$.

The specific heat of hydrochloric acid solutions, even of the most concentrated, is always less than that of the water itself which they contain.

Sodium Chloride, NaCl + n Aq.—The formula is $C = 18n - 20{\cdot}45 + \frac{481}{n} - \frac{2100}{n^2}$.

Addition of water to a solution of chloride of sodium always occasions a diminution of the molecular specific heat. A solution containing about 18 molecules of water has the same molecular heat as the water which it contains; in more dilute solutions the molecular heat is less than that of the water contained in them.

Sugar, $C_{12},H_{22}O_{11}$ + n Aq.—The experiments lead to the conclusion that the molecular heat of sugar in the liquid state is 147, and its specific heat 0·430. The molecular heat of any solution of sugar will then be the sum of the molecular heats of the water and the sugar they contain.

Solutions in Sulphide of Carbon.

Specific heat of sulphide of carbon	0·238
Molecular heat	18·1

Solutions of the following substances in sulphide of carbon were examined, namely, *sulphur*, *phosphorus*, *bromine*, and *iodine*. The experiments show that the diminution of specific heat resulting from solution, or from dilution, is either not observable at all, or is slight (sulphur and phosphorus). The molecular heat of these solutions, above all, never becomes inferior to that of the solvent alone.

General Observations.—According to Kopp and Regnault, the molecular heat of a compound, and of an alloy, is always nearly equal to the sum of the molecular heats of its constituents. As regards aqueous solutions, it appears, however, that while solutions of sugar and ammonia are in conformity with Kopp and Regnault's approximate law, the molecular heat of mixtures of alcohol and water is always above the sum of the molecular heats of its constituents. In the case of most saline solutions, on the other hand, a diminution of molecular heat takes place.

If all solutions behaved in a similar manner, this anomaly might be simply due to the difference in physical condition between the solid and the liquid state; but as various solutions behave very differently, it must be due to a chemical cause. Thus we may assume that every change of temperature involves a change in the chemical constitution of the solution, such chemical work being either a source of absorption or of disengagement of heat. This, of necessity, augments or diminishes that which must be transmitted to the solution to change its temperature, and consequently the heat alters its apparent specific heat. Pfaundler, who has previously* expressed this same idea, has more recently† even proposed the study of the specific

* J. pr. Chem., vol. ci, p. 507. † Zeitschr. f. Chemie [2], vi, p. 66.

heats of solutions and their elements as a means of determining the degree of dissociation produced in them by heat.

It appears useful to enunciate or recall these theoretic ideas at the present time, even though it may be difficult to explain the opposite effects observed in mixtures of alcohol and of sulphuric acid with water, by this hypothesis of a change in the chemical constitution of the solution according to temperature. A. D.

On the Spectra of Carbon. By W. MARSHALL WATTS, D.Sc.*

THIS paper is the sequel to one which appeared in the "Philosophical Magazine," for October, 1869. The author gives the readings of the lines obtained by passing the spark from an induction coil through carbonic acid or carbonic oxide, a Leyden jar being included in the circuit. These readings he converts into wave-lengths, by means of an interpolation curve, founded on the observation of twenty lines whose wave-lengths are given in Ångström's map.

S. W.

On the Examination of the Bessemer Flame with Coloured Glasses and with the Spectroscope. By J. M. SILLIMAN.†

PROFESSOR SILLIMAN treats his subject under two headings—1st, the examination of the Bessemer flame with coloured glasses; and, 2nd, with the spectroscope. The results of the first part are confirmatory, with slight variations, of Rowan's observations. The author, in his experiments, used three coloured glasses, two light yellow, and one blue, through which the sunlight appeared of a deep purplish-blue tint. In the second part, after narrating the work done by Roscoe and Lielegg, the writer describes his own instrument, and the order observed in his work. The instrument is provided with a single equiangular prism and a reflected scale. In the course of his experiments he made the important observation that a movement of the eye before the eye-glass occasioned a similar movement of the lines of the spectrum along the scale, on which their position could be made to differ more than half a degree. To obviate it, however, the position of the eye before every reading was adjusted so as to bring the sodium line always on 50°. He has failed to find some of the lines given by Lielegg, but has detected others not given by him. The lines of which Professor Silliman gives readings are thirty-three in number:—

1st Period: 23½, 35, 50, 135.

2nd Period: 23½, 35, 43, 44, 44½, 45½, 46, 47½, 48½, 50, 52, 53, 56, 56½, 61½, 62, 62½, 63, 65, 66½, 67½, 70, 72, 120, 135.

* Phil. Mag. [4], xli, 12. † Phil. Mag. [4], xli, 1.

3rd Period: 23½, 35, 43, 44, 44½, 45½, 46, 47½, 48½, 50, 51½, 52, 53, 56, 56½, 57, 61½, 62, 62½, 63, 65, 66½, 67, 67½, 70, 72, 100, 102, 103, 105, 108, 135.

Amongst the dark bands the most intense were—

44—46, 51—55, 56—58, 62—64½,

others at

33—34½, 36½, 37½, 38½, 40, 68, 72.

The author discusses at some length the theory adopted by Wedding, that the absence of the spectrum at the beginning and end of the blow is due to the small quantities of the bodies volatilized, and inclines to consider that, in the case of the manganese spectrum, the lack of sufficient flame may account for its sudden disappearance at the termination of a blow. In conclusion, the author suggests the use of more delicate instruments, and augurs much good to the science of spectrum analysis by careful observations of the Bessemer flame. S. W.

On the Examination of the Bessemer Flame with Coloured Glasses, and with the Spectroscope. By J. SPEAR PARKER.*

THE combination of coloured glasses, used by Mr. Parker in his investigation, consisted of one light cobalt-blue, and one amber coloured. He does not approve of a deep blue glass, as the flame under such circumstances merely shows varying shades of crimson. With regard to the utility of using coloured glasses, the author considers that they are of advantage to the inexperienced, and tend to preserve the eyes, but that the skilled workman is able to detect the change with surprising accuracy with the naked eye.

In his spectroscopic examination Mr. Parker made use of a direct vision instrument of five prisms. The spectrum obtained by him does not vary from that obtained by other investigators. The presence of an absorption-band is considered by him as merely owing to the effect of contrast. He thinks that the first group of green lines, and the prominent red group, cannot be referred to manganese. He has observed the most prominent bright lines, especially the two green groups, when the metal is poured out of the converter into the ingot-mould, a large flame appearing simultaneously. The writer thinks the spectrum in this case "is caused by the *graphite*, with which the moulds are lined to fill up any cracks or crevices, and thus facilitate their ready separation from the ingots, and must, therefore, be due to the combustion of carbon by the air carried down with the stream of metal at an intense white heat."† S. W.

* Chem. News, xxiii, 25.

† Observations on the two preceding papers have been published by Dr. W. M. Watts (Chem. News, xxiii, 49).

On the Electromotive Force on Contact of Different Metals. By E. EDLUND.*

IN a previous paper the author has shown that if a voltaic current traverses an electromotor in the same direction as the current produced by the electromotor itself, an amount of heat is absorbed in the electromotor which is proportional to the electromotive force multiplied by the intensity of the current. If the current is in the opposite direction, a quantity of heat is produced which is proportional to the same product. For the same intensity of current, the quantities of heat absorbed or produced in various electromotors are, therefore, proportional to the electromotive forces. If then a current is traversing a conducting wire consisting of two different metals, there must be an alteration of temperature at the place of junction, because there exists at that place an electromotive force. Now experiment has shown that heating or cooling occurs at the place of contact between two metals when a voltaic current traverses it, and that this alteration of heat is, as theory requires, proportional to the intensity of the current. Hence the measurement of the quantities of heat absorbed or produced by the voltaic current gives a determination of the magnitude of the electromotive forces produced by the contact of the metals.

Now the quantities of heat produced by the passage of the current are of two sorts. Firstly, heat is produced owing to the voltaic resistance of the wire, in quantity proportional to the square of the intensity of the current; while, secondly, an amount of heat proportional to the intensity of the current, is either absorbed or produced at the point of contact of the two wires.

Now let s be the intensity of the current and m and n two constants, then s^2m will be the heating effect due to the voltaic resistance, and $\pm sn$ the heating or cooling due to the action at the point of contact of the two metals. Further, suppose the index to have moved $A + a$, divisions with the current passing in one direction, and $A + a'$ division with the current passing in the opposite directions.

We shall have $s^2m \pm sn = A + a$

$$s^2m \mp sn = A + a'$$

$$\text{and } \pm 2sn = a - a'.$$

The difference between the two stationary positions of the index, when the current passes in opposite directions, is thus a measure of the heat produced or absorbed at the point of contact of the two metals.

Experiments made on this principle gave the following electromotive series: Bismuth, argentan (German silver), platinum, copper and iron, —silver and zinc being undecided. The relative numerical values are:—

* Phil. Mag. [4], xli, 18.

Bismuth-copper	141·3
Argentan-copper	15·57
Platinum-copper	7·37
Copper-iron	17·83

Experiments were next undertaken in order to ascertain the thermoelectric relations of these combinations. The results, when calculated for a difference of temperature of 10° and a conductivity = 100, yielded the following deflections of the magnetometer:—

Bismuth-copper, the deflection		92·27
Argentan-copper	,,	23·18
Platinum-copper	,,	8·23
Zinc-copper	,,	0·90
Silver-copper	,,	0·63
Copper-iron	,,	24·93

The thermoelectric series of these metals is, therefore, the following: Bismuth, argentan, platinum, zinc, silver, copper and iron. In the former series the position of silver and zinc could not be determined, owing to the slight effect produced by their combination with copper; the other metals are, however, in the same order in both series. If the numbers in both series be calculated so as to be equivalent for one of the combinations—copper-iron for example,—we obtain—

	Thermoelectric series.	Electromotive series.
Bismuth-copper	92·27	197·6
Argentan-copper	23·18	21·77
Platinum-copper	8·23	10·30
Zinc-copper	0·90	—
Silver-copper	0·63	—
Copper-iron	24·93	24·93

The combination bismuth-copper was once more examined in regard to its thermoelectric and electromotive forces; the results agreeing substantially with the above. It will thus be seen that, although the number for the combinations argentan-copper and platinum-copper are nearly equal in both series, yet, as shown by the combination bismuth-copper, the electromotive and thermoelectric forces are not proportional to one another.

According to Seebeck, these metals have the following order in the electric tension series:—silver, platinum, copper, iron, bismuth, and zinc. There is thus no similarity between this series and the other two; and hence it is highly probable that the electrical tension does not depend exclusively on the contact between the two metals, but on the layer of gas or water which is condensed on their surfaces. On the other hand, the metals which in contact with each other produce the

greatest electromotive force, also produce the most powerful thermo-electric current when the place of contact is heated; but these thermo-electrical currents are not in all combinations proportional to the corresponding electromotive forces.

A. D.

On some Hydro- and Thermo-electric Forces, reduced to the Siemens' Unit Resistance and Weber's Unit of Current. By T. KOHLRAUSCH and M. A. AMMANN.*

THE electromotive forces are expressed according to Ohm's law $e = wi$; where the resistance w is expressed in Siemens's units, the intensity i in the magnetic unit of Weber. The electromotive forces thus measured are given as Siemens-Weber.

Hydro-electric circuits, measured by tangent compass—

1. Grove's element (sulphuric acid, 1·06 sp. gr. zinc freshly amalgamated) = 19·98. Siemens-Weber.

2. Daniell's element (sulphuric acid and zinc, as above) = 11·71. Siemens-Weber.

3. Copper-zinc element (sulphuric acid and zinc as above) = 10·82. Siemens-Weber.

Thermo-electric circuits, measured by Poggendorff's compensation method. The metals were hard-drawn wires of about 1 millim. diameter, one junction having a temperature of about 16° C., the other one of $t°$ higher, the electromotive force e (in Siemens-Weber) is found.

For German silver and copper—

$$e = 0{\cdot}0001549t + 0{\cdot}000000291t^2.$$

For copper and iron—

$$e = 0{\cdot}0000969t + 0{\cdot}0000000149t^2.$$

For German silver and iron—

$$e = 0{\cdot}0002476t + 0{\cdot}000000196t^2.$$

The values of e thus caclulated agree very closely with those found by direct observation.

A. D.

"*Polarization of Metallic Surfaces in Aqueous Solutions, a new Method of obtaining Electricity from Mechanical Force, and certain relations between Electrostatic Induction, and the decomposition of Water.*" By C. F. VARLEY.†

THE author describes an apparatus by which he obtains electric currents from polarized surfaces of mercury; by a mechanical arrangement he alters the relative amount of the polarized surfaces of the elements of

* Phil. Mag. [4], xli, 157.

† Proc. Roy. Soc., xix, 243.

the battery, and by such change obtains electrical currents. The second part of the paper refers to the electrostatic capacity of platinum plates in dilute acid and water. C. G.

"*On a constant form of Daniell's Battery.*" By Sir WILLIAM THOMSON.*

THE author employs the following form of element. :—

The cell is of glass; in form cylindrical, or rectangular, with a flat bottom. The depth may be 10 centimetres or more, where permanence and ease of management are of more importance than very small internal resistance. A disk of thin sheet copper is placed at the bottom of the trough; to this is soldered or riveted a copper wire, insulated with gutta-percha, passing up vertically through the liquid; and with this the zinc of another element can be connected. A grating of zinc, to which is attached a suitable electrode, is supported in the upper part of the jar.

A glass tube (the *charging tube*) a centimetre or more in internal diameter, expanded to a funnel at the top, is supported so as to rest with its lower open end about one centimetre above the copper. A glass siphon with cotton-wick core, or a capillary glass tube, is placed so as to draw liquid gradually from a level about a centimetre and a half above the copper, and to discharge the same at a level slightly higher than the upper surface of the zinc grating.

The jar is then filled with semi-saturated solution of zinc sulphate.

To put the cell in action, finely broken crystals of copper sulphate are placed in the funnel at the top of the charging tube. The liquid stratum below the aperture of the tube, thus becomes saturated with copper sulphate.

The cell is now ready for use, and may be kept so by occasionally pouring in fresh water, or water one-quarter saturated with zinc sulphate, at the top of the cell, to replace the liquid removed by the siphon from near the bottom.

The author recommends the use of specific gravity bulbs kept floating in the liquid, to show with precision, whether the liquid added from time to time should be pure water, or water more or less saturated with zinc sulphate. The best results are obtained when the liquid in contact with the zinc is a little less than half saturated with zinc sulphate.

The siphon extractor must be arranged to carry off all the water of crystallisation of the copper sulphate decomposed in the cell, and enough of water besides to carry away as much zinc sulphate as is formed in the use of the battery. C. G.

* Proc. Roy. Soc., xix, 253.

On Solutions for Electro-deposition of Copper and Brass. By W. H. WALENN*.

A SOLUTION containing one pound of cupric sulphate and one pound of sulphuric acid to the gallon of water, deposits the metal in a solid compact mass, with a somewhat botryoïdal surface. The addition of 1 ounce of zinc sulphate (as recommended by Napier) annuls this botryoïdal form, and renders the deposit tough, compact, and even. From a solution containing a greater proportion of zinc sulphate the metal is deposited in tufts of needles standing at right angles to the surface of the metal. Ordinary electro-brassing solutions show the same peculiarity in even a more marked degree, and this makes it impossible to produce a good deposit of more than 0·01 to 0·03 inch in thickness. This form of deposit is owing chiefly to a copious evolution of hydrogen taking place during its formation. However, the author has found that by employing a solution containing both the oxides and the cyanides of the constituent metals, together with some neutral ammonium tartrate, this evolution of hydrogen may usually be avoided, or, should it, nevertheless, take place to a slight extent, it may be entirely stopped by the addition of some cupric ammonide. Such a solution yields brass of a uniform character, and the deposit, which may be obtained of any thickness desired, is tough, and has a compact, even texture. As there is no evolution of hydrogen, no electric force is wasted, and perfect results may be obtained with a single Wollaston's or Smee's cell.

A. D.

Inorganic Chemistry.

On the Action of Water on Iron and of Hydrogen on Oxide of Iron. By H. SAINTE-CLAIRE DEVILLE.†

THE following researches into the action which water-vapour exerts upon iron have been carried out on the same plan as that by which the author has established that the progressive decomposition of a gaseous substance is characterized by a dissociation-tension, which, like the tension of a vapour, can be measured in millimetres of mercury.

Perfectly pure iron was subjected to the action of water-vapour of known tension and temperature, the iron itself being also maintained at

* Phil. Mag. [4], xli, 41.

† Ann. Ch. Pharm., clvii, 71, from Comptes Rendus, lxx, 1105, 1201, and lxxi, 30.

a constant temperature throughout an experiment, which in different experiments could be varied between 150° C. and about 1600°. The apparatus employed consisted of a porcelain tube containing the iron, and communicating at one end freely with a glass tube-retort containing water to furnish the vapour, and at the other with a manometer. By means of a lateral tube at the upper part of the manometer, the interior of the apparatus could be placed in communication with a Geissler's or Sprengel's pump, and by another arrangement it could be filled when required with pure hydrogen or other gas.

The iron employed was porous, and obtained by reducing the red oxide with hydrogen. The oxide employed was, of necessity, the magnetic oxide, which was obtained by the action of steam on reduced iron.

The glass retort-tube was kept either in ice or in water of constant temperature flowing from the Paris mains, the temperature being maintained always lower than that of the air, in order that condensation of aqueous vapour might not occur in any other part of the apparatus.

For all temperatures to which the iron was exposed below 300°, an oil- or a mercury-bath, heated by a gas-flame provided with Schlösing's regulator, was used. For the constant temperatures 360°, 440°, 860°, and 1040°, the vapours of boiling mercury, sulphur, cadmium, and zinc were respectively employed. The cadmium was heated in a mercury-bottle, to which, near its neck, was fitted a gun-barrel, serving to condense and return the cadmium to the bottle, while another iron tube passed through the bottle within which the porcelain tube was placed. The zinc was heated in a black-lead crucible, such as is used in the manufacture of steel, through the body of which an earthen tube passed to receive the porcelain tube, and to the lid of which was attached another upright earthen tube, to condense and return the zinc to the crucible. The iron bottle or the crucible was placed in a furnace heated by petroleum, and the temperature of which was kept constant by graduated stop-cocks to regulate the supply of oil. Lastly, for all temperatures above 1040°, the porcelain tube was exposed to the direct regulated flame of the petroleum, and by this means the temperature at which iron melts was reached, which is below that at which a thick refractory porcelain tube softens.

The following results have been obtained:—(1.) On subjecting any quantity of iron to the action of water-vapour, the iron continues to oxidize, until, at a fixed temperature, the tension of the liberated hydrogen becomes constant in value. (2.) The point of maximum tension for a given temperature having been reached, the withdrawal of some of the gas, so as to diminish the pressure, is rapidly followed by a restoration of the tension caused by the decomposition by the iron of a new quantity of water, which evaporates from the retort; or, the pressure being

increased by sending some hydrogen into the apparatus, the pressure rapidly returns to its original amount by a reduction of some oxide of iron by the hydrogen, with formation of water, which condenses in the retort. (3.) The point of maximum tension for a given temperature of the iron having been reached, the space in which the moist hydrogen is enclosed can be brought to any desired temperature, without the tension of the gas changing—provided, that is, that the temperature is not so low as to cause any water to condense. For example, when heat is applied to the apparatus, the tension of the gas is preserved by some of the hydrogen *condensing* on the oxide of iron. (4.) When the tension of the water-vapour is maintained constant and equal to 4·6 mm., corresponding to a temperature of 0°, and the temperature of the iron is made different in different experiments, the tension of the hydrogen is found to be less as the temperature of the iron is higher. At a temperature of 200°, the tension of the moist hydrogen = 100 mm.; at 260° it is 68·8 mm.; at 360°, 45 mm.; at 440°, 30·4 mm.; at 860°, 17·7 mm.; at 1040°, 13·5 mm.; and at the melting point of iron, 9·7 mm. The lower the temperature of the iron, the more slowly does the tension reach its maximum, or—if the tension of the gas has been raised beyond the maximum for the temperature of the iron—the more slowly does it sink to this. (5.) When the tension of the water-vapour is maintained constant and at the maximum corresponding to some other temperature than that of 0°, it is found that (*a*) the higher the tension of the water-vapour, the higher is the tension of the hydrogen, the temperature of the iron remaining constant; (*b*) an increase in the tension of the water-vapour causes more than a proportionate increase in the tension of the hydrogen; and (*c*) the difference of the increase of the respective tensions becomes less and less as the temperature of the iron is made higher: thus, with the iron at 200°, the increase (supposed to be uniform) of the tension of the hydrogen, corresponding to an increase of 1 mm. in that of the water-vapour, is 29·8 mm., while with the iron at about 1600° it is only 0·56 mm. (6.) All the laws as to the formation of hydrogen by heating together a small quantity of water and a large quantity of iron hold good, just the same, and with the same constants for given temperatures, when a small quantity of hydrogen is allowed to act on a large quantity of oxide of iron.

The most perfect analogy exists between the phenomena which form the subject of this memoir and those of hygrometry, the iron at a given temperature comporting itself like water, and the hydrogen as the vapour evolved from it, as a consideration of the results recorded under (1), (2), and (3) will at once show, the principle involved in (3) having a manifest analogy with the principle of Watt. From (5 *c*) it may be assumed that at a sufficiently high temperature of the iron the increase in the tension of the hydrogen would = 0; in this case the tension of

the hydrogen would only be added to that of the water-vapour, as if it were an indifferent gas, and the hygrometric law relating to a mixture of gases and vapours would still find its application to the phenomena here investigated. The phenomena of combination, decomposition, dissolution, and passage to the solid, liquid, or gaseous state, being all attended with a disengagement or an absorption of latent heat, have, no doubt, a common cause.

Berthollet's hypothesis as to the *influence of mass* does not serve to explain the phenomena of the action of iron upon water-vapour; for, 1stly, the tension of the hydrogen is quite independent of the quantity of iron; and 2ndly, as the masses or relative weights of the hydrogen and the water-vapour are respectively proportional to their tensions, it is evident, from (5 *b*), that the proportion between the weights of the gaseous substances entering into a reaction does not affect its results.

From (4) it most unexpectedly appears that the higher the temperature of the iron, the smaller is the quantity of water which it decomposes, or, in the figurative language of chemistry, the less is the affinity it shows for the oxygen of water. Not only is this the case, but, as again unexpectedly appears from (5 *c*), it is at the lowest temperatures of the iron that the tension of the hydrogen most rapidly increases when the tension of the water-vapour increases.

The following facts are incidentally communicated in the memoir:—(1.) Iron is distinctly though slowly attacked by steam at 150°, which may perhaps account for the singular erosion by distilled water of the iron of the boilers of steam vessels. (2.) The oxide of iron obtained by acting on iron by water-vapour at a temperature of 440°, and removing the hydrogen as fast as it is produced, has a composition corresponding to Fe_4O_5; it is amorphous, black, magnetic but not polar, scarcely attacked by concentrated hot or cold nitric or sulphuric acid; it is readily soluble in cold hydrochloric acid, without sensible evolution of hydrogen, and forms a deep-brown solution, yielding a black precipitate with potash. (3.) By the action of steam on spongy platinum mixed with potassium cyanide at a dull red heat, much hydrogen is disengaged, and among other products a large quantity of potassium platinocyanide is formed.

E. D.

On the Condition of Carbon and Silicon in Iron and Steel. By G. J. Snelus.*

The author, after quoting the views held by Berzelius, Karsten and Rammelsberg, Von Mayrhofer, and others, who have assumed the existence of definite chemical compounds of iron and carbon in the

* Journal of the Iron and Steel Institute, Feb., 1871, p. 28.

formulæ published by them, proceeds to describe his own investigations.

He employs the following mechanical means to obtain the graphitic substance. By means of a penknife he was able to remove the graphitic scales from slowly-cooled Bessemer pig. ·0345 grm. of the material thus obtained was heated in a current of oxygen and yielded—

Residue, 0·0015 grm. (consisting of sand with a mere trace of Fe_2O_3) CO_2 0·104 grm. = 0·0283 C.

By means of a magnet the author separated, as far as possible, the iron from the graphite in finely powdered pig-iron.

0·1045 grm. of this graphite, after combustion, gave a residue weighing 0·012 grm. (containing 0·008 grm. Fe_2O_3 and 0·004 grm. sand, &c.). The CO_2 formed weighed 0·3505 grm. = 0·0955 grm. C.

Lastly, 0·1415 grm. kish purified with hydrochloric and hydrofluoric acid yielded 0·518 grm. CO_2 = 0·14154 grm. C., and left no weighable residue.

In all these cases the author concludes that the graphite scales thus removed contained no iron, the small quantities found in the analyses being due to accident.

Advantage was also taken of the great friability of graphite. Borings from grey Bessemer pig were sifted through a fine silk sieve. Pig containing 3·008 per cent. gave in the fine dust 7·605, and another sample containing 4·071 per cent. yielded in the dust 9·288. By availing himself of the lesser density of graphite and levigating the finely-sifted borings, the author obtained the following results:—

		Original pig.	Siftings.	Levigated powder.
(1) Bessemer pig	Graphite	3·190	7·79	21·274
	Combined carbon	0·2	0·17	—
(2) Middlesborough forge pig.	Graphite	2·650	7·015	41·329
	Combined carbon	0·35	0·30	—

"These results clearly show that in grey pig-iron the carbon exists in two states, and that the free, or graphitic carbon, can be more or less separated by mechanical means, while the so-called 'combined carbon' decreases in the separated portions in the same ratio as the residual iron."

Finally, the author holds that the absorption of carbon by iron is rather a case of solution than of definite chemical combination.

Silicon.—This element invariably occurs in pig-iron, and even in steel and wrought iron the author has never found it entirely absent. In good Bessemer and in tool steel it rarely exceeds two or three parts in 10,000 of iron. By employing the methods quoted above, the author obtained the following results:—

Amount of silicon per cent. in—

	1. Original pig.	2. Fine siftings.	3. Levigated powder.
West Cumberland Bessemer pig ..	2·419	2·380	—
Dowlais Bessemer pig	3·849	3·639	3·158
Middlesborough pig.....	1·815	1·610	1·219

Here the silicon, unlike the graphite, does not increase in the finer portions, but diminishes. It remains with the iron just as the "combined" carbon does. Hence the author concludes that the silicon is in combination or in solution in the iron, and is never—except perhaps in an exceptional case—found in the free state.

C. G.

The Composition of the Ferric Iodates. By CHICHESTER A. BELL.*

THE author describes some experiments undertaken to facilitate the preparation of a ferric iodate, to be used as a substitute for ferrous iodide. The compound, $Fe_2O_3.2I_2O_5,8H_2O$, formed by precipitating a solution of iron alum by an excess of potassium or sodium iodate, has been used with success in medicine; but appears to alter by exposure to air. A compound which has the advantages of being anhydrous, perfectly stable, tasteless, and odourless, is obtained as a fine yellow precipitate by heating a solution in 5 or 6 parts water of ferrous iodide, obtained in the usual manner from 2 parts iodine, with 2 parts potassium chlorate dissolved in a little hot water, and $1\frac{1}{2}$ parts strong nitric acid. The formula $Fe_2O_3,3I_2O_5$, or $Fe(IO_3)_3$, expresses its composition. It contains 9·64 per cent. Fe, and 65·57 per cent. I; the crystallised ferrous iodide of the Pharmacopœia containing about 15 per cent. Fe and 67 per cent. I. It is scarcely soluble in cold water, and but slightly so in strong nitric acid.

The use of but small quantities of nitric acid in the above oxidising mixture produces compounds less rich in iodic acid; one, of a deep red colour, appears to contain Fe_2O_3,I_2O_5, dried at 100° C.; it decomposes, however, during washing. These basic mixtures are converted into the triiodate by digestion with warm dilute nitric acid.

W. H. D.

On Nickel Chromate and Ammonio-nickel Chromate. By E. A. SCHMIDT.†

NICKEL chromate having the formula $3NiO.CrO_3+6H_2O$ (Fresenius, *Zeitschr. f. Chemie.* [2] VI. 30) is formed only when the precipitate is

* Pharm. Journ. Trans [3], I, 624.

† Zeitschrift für Chemie [2], vii, 31, from Ann. Ch. Pharm. clvi, 19.

thrown down in presence of excess of nickel-salt, as, for instance, on mixing boiling solutions of 2 mol. of nickel sulphate and 1 mol. of potassium chromate. When, on the other hand, the chromate is in excess, precipitates containing less nickel are thrown down under otherwise similar conditions: with 2 mol. potassium chromate and 1 mol. nickel sulphate, the author obtained the salt $5NiO.2CrO_3+12H_2O$, and with 4 mol. of the chromate to 1 mol. of nickel sulphate the salt $2NiO.CrO_3+6H_2O$. No salt containing less nickel than the last was obtained; on the contrary, by employing 10 or 12 mol. potassium chromate to 1 mol. nickel sulphate, precipitates were thrown down, the composition of which lay between $5NiO.2CrO_3$ and $2NiO.CrO_3$. When basic nickel chromate, still moist, is triturated to a thin pulp with ammonia, and gaseous ammonia is passed in till the brown colour completely disappears, ammonio-nickel chromate is deposited in the form of a yellowish-green crystalline powder. Further quantities of the same salt are obtained by placing a few crystals of neutral ammonium chromate in the mother-liquor. Large and well-formed prismatic crystals are produced when the ammoniacal solution is covered with a layer of alcohol; they are yellowish-green, dichroic by transmitted light, and undergo decomposition in the air, and more rapidly on warming, giving off ammonia. Malaguti and Sarzeau assign to this salt the formula $NiO.CrO_3.3NH_3+4H_2O$; but the author found the salt to be anhydrous, and to have the composition expressed by the formula $NiO.CrO_3.3NH_3$.

J. R.

On the Alkaline Reaction of Silver Oxide and Silver Nitrate.
By A. Vogel.*

The older statements of the alkalinity of silver oxide are confirmed by Dr. Vogel, who obtained the oxide by adding lime-water to a solution of silver nitrate, which was distinctly acid; the silver nitrate was kept in excess. The liquid from which the oxide was removed had still a feebly acid reaction. Carefully washed, the damp silver oxide gave distinct indications of alkalinity with litmus- and turmeric-paper. Several samples of commercial lunar caustic showed an alkaline reaction with litmus-paper, but Dr. Vogel thinks that the lunar caustic may be regarded to some extent as a basic salt, inasmuch as a solution of crystallised silver nitrate lost its acid reaction by boiling with silver foil or silver oxide, and became alkaline.

W. H. D.

* N. Repert. Pharm., xx, 93.

Mineralogical Chemistry.

On the Chemical Composition and Microscopic Constitution of certain Cornish Rocks. By J. ARTHUR PHILLIPS.*

"KILLAS" is the name applied by Cornish miners to all sedimentary cleavable rocks. Their geological age has not been determined beyond that they belong to the palæozoic era, and it is believed that they are of Devonian age. They enclose five large and several smaller "islands" of granite, and are, as well as the granite itself, traversed by dykes of granitic and porphyritic rock called *elvans*, by trap dykes, by copper and tin lodes, and by various cross-courses, including *flucans*, or fissures filled with clay. Typical killas is a grey, bluish-grey, or greenish-grey clay-slate, and, when weathered, is brownish-yellow or buff. It is usually exceedingly fissile with the planes much contorted but is often more compact near its junction with the granite. The sections examined in the microscope by "a low power" were magnified 60, or by a "high power" about 400 linear.

I. *Killas from Polgooth Mine, adit level*, sp. gr. = 2·60. This is a very soft slate of a light-grey colour marked in places with a darker shade or yellow tinge. By transmitted light under a low power, thin sections exhibit no structure but appear as a milky-white mass, enclosing moss-like semi-crystalline markings of a brownish-green and traversed by fissures filled by crystalline transparent quartz. With a high power it is found to be composed of an aggregate of minute granules intimately blended together without definite outlines, and to enclose some grains of oxide of iron and apparently fragments of hornblende, and some patches of a chloritic mineral.

II. *Killas from Polgooth Mine*, 80 *fathoms level*, sp. gr. = 2·74. This specimen, much harder than the above, is of a grey colour, strongly marked with reddish-brown. Here the microscope detected no difference excepting that the grains of oxide of iron were larger, but less numerous, and that there were fewer of what appeared to be broken crystals of a hornblendic mineral. The granular fragments are larger and more distinct, their larger surfaces being nearly parallel with the planes of cleavage of the slate. The chloritic mineral is again very abundant, and peculiar markings were observed about its margin.

III. *Killas from Polgooth Mine*, 100 *fathoms level*, sp. gr. = 2·73. At this depth it is much harder than that found at shallower levels, is of a greenish-grey, slightly streaked and spotted with yellow. The sections resemble those from the 80 fathoms level, but contain no hornblende and fewer chloritic patches.

IV. *Killas from Polmear Mine*, 40 *fathoms below the surface*, sp. gr. = 2·68. This clay slate is much contorted, dividing readily in curved

* Phil. Mag. [4] xli, 87.

laminæ, with glossy surfaces bearing wavy lines resembling minute ripple marks. It is of a medium grey, and slightly yellow in places. Its sections resemble those of the Polgooth specimens. Granules of quartz are disseminated through the finely-grained matrix, which derives its greenish tint from chlorite, and which is minutely divided by a system of markings made up of pairs of parallel lines, each about $\frac{1}{1000}$ th of an inch long, and $\frac{1}{6000}$ th of an inch apart.

V. *Slate from "Sanctuaries" near St. Austell*, sp. gr. = 2·52. This is light grey and buff in colour and appears to be weathered. It divides with difficulty into laminæ, the surfaces being without polish. It is divided by headings variously coloured, apparently by infiltration of water containing oxide of iron.

VI. *Killas from Dolcoath Mine*, 215 *fathom level*, sp. gr. = 2·71. This rock is exceedingly hard, the cleavage imperfect, and its prevailing colour dark-grey. Freshly fractured surfaces exhibit numerous minute, brilliant, indistinct crystals probably of some hornblendic mineral. With a low power its sections appear to be made up of transparent angular particles, giving colours with polarised light; the greenish patches disseminated through the mass are probably chlorite. With a high power, are seen, black grains of magnetite and titaniferous iron, and fanlike aggregations of transparent acicular crystals, often diverging from a particle of oxide of iron. Similar crystals also cross each other in all directions, and are probably hornblende or schorl. Mechanically embedded are rounded fragments of mica, and of a semi-translucent mineral not sufficiently opaque for oxide of iron.

VII. *Killas from Botallack, Penzance, surface near lode*, sp. gr. = 2·95. This is a very hard, dark greenish-grey rock, containing minute crystals of pyrites; its cleavage being to a great extent obliterated by metamorphism: it breaks into roughly tabular masses, whose planes approximate to those of original cleavage. The low power shows an amorphous base, often green, due probably to chlorite, and enclosing transparent crystals, and crystalline patches, often fringed with acicular crystals, which give brilliant colours with polarised light. With a high power, long slender crystals, probably of apatite and minute triclinic crystals, possibly of axinite, are seen.

VIII. *Rock from Botallack*, 130 *fathoms*, sp. gr. = 2·82. A very dark green specimen with traces of lighter shade and no cleavage, is slightly magnetic, and encloses in places minute crystals of pyrites. The grains of iron oxide are more numerous than in specimens obtained nearer the surface. It contains fewer long crystals than the surface rock, and is traversed by minute veins of quartz enclosing transparent acicular crystals, probably of hornblende. From its physical constitution and the large amount of magnesia it contains, it may be regarded as an impure serpentine.

IX. "*Best roofing slate*," *Delabole*, sp. gr. = 2·81. Whilst under a low

power this slate shows no distinct structure, but is thickly dotted with dark spots, with a high power numerous clusters, about $\frac{3}{1000}$th of an inch in diameter, of reddish-brown crystals appear. These result from the aggregation of several hexagonal plates of, according to Mr. Sorby's examination, more or less altered specular iron. The matrix is, moreover, traversed in all directions, but especially in planes parallel to the cleavage, by long transparent crystals that are brilliantly coloured by polarised light. Both brown and white crystals have been formed *in situ*.

X. *Diorite*, "*Sanctuaries*," *St. Mewan*. sp. gr. = 2·97. This rock is of a dark green colour verging on black, is exceedingly hard and tough, distinctly crystalline and magnetic. These sections exhibit unmistakable evidence of extensive alteration. The felspar does not generally present any distinctive characteristics, although in a few instances the parallel striping peculiar to triclinic varieties was observed. The rock also contains semi-transparent yellowish-brown crystals, probably hornblende, a green mineral of fibrous structure which is believed to be a variety of hornblende, many black grains of oxide of iron, some well-defined hexagonal crystals, probably apatite, and an abundance of a green chloritic mineral. This diorite has probably undergone much alteration.

XI. "*Greenstone*," *Blowing-House Hill*, *St. Austell*, sp. gr. = 2·89. This stone is very similar to the "Sanctuaries" rock, but is of a somewhat duller aspect, and is divided by a series of oblique cross headings, which impart to it a tendency to divide into rhomboidal masses; it is also less decidedly crystalline, and exhibits a grain resembling that of some varieties of metamorphosed schist. The sections shew a compact felspathic matrix enclosing a few indistinct crystals of felspar, together with large quantities of the greenish chloritic mineral observed in the St. Mewan diorite, from which the greenstone differs but little in composition. The greenish mineral is arranged in approximately parallel bands and patches, many of the latter appearing to be partially decomposed hornblende crystals, and, though retaining at their centre to a certain extent their original structure and colour, have at the edges been transformed into chlorite or an allied mineral. The rock also contains many black grains of oxide of iron, and some hexagonal crystals, probably of apatite. It is believed to be an altered clay-slate.

XII. *Serpentinous rock*, *Menheniot*, sp. gr. = 2·77. This is a moderately hard stone of a dark green colour, has a somewhat crystalline fracture and schistose structure, and is slightly magnetic. It occurs more or less intermixed with clay-slate, and beds of unaltered slate are found interstratified with it. It exhibits numerous resinous headings, many of which are coated with asbestos, with fissures containing calcite.

Reniform concretions of saponite are frequently found in a clay, apparently resulting from the decomposition of the principal rock. The microscope shows a highly metamorphosed rock consisting of an amorphous matrix, porphyritically enclosing yellowish-brown or green patches with indistinct crystalline forms, evidently pseudomorphs, with many grains of magnetite and crystals of what is probably schiller-spar or diallage.

XIII. *Serpentine, Lizard*, sp. gr. = 2·59. The specimen is of a very dark green colour, in places verging on black and thickly spotted with red; it has a coarsely granular structure, is without any indication of foliation, and encloses imperfectly developed crystals.

XIV. *Orthoclase*, "*Glass Mine*," *Roche*, sp. gr. = 2·55. This yellowish-white felspar occurs in granite containing considerable quantities of schorl, and is traversed by veins of milky quartz enclosing tourmaline and cassiterite. Prof. Miller, of Cambridge, examined it crystallographically and pronounced it to be a mono-clinic felspar.

The following table exhibits the mean results of the analyses of these rocks:—

	H_2O.	SiO_2.	TiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	Mn_3O_4.	CaO.	MgO.	K_2O.	Na_2O.
.	4·08	60·42	—	0·21	20·835	8·17	1·89	0·41	1·71	trace.	0·77	1·55
I.	3·63	63·10	trace.	trace.	20·15	3·51	2·955	trace.	1·27	trace.	0·95	3·14
II.	3·265	50·915	trace.	—	29·785	13·415	4·92	trace.	1·62	—	0·93	4·08
								Fe_2S_3				
V.	6·58	49·265	trace.	—	18·00	12·68	8·55	0·82	2·13	trace.	0·565	0·745
V.	6·16	53·30	trace.	trace.	21·725	6·015	4·28	—	trace.	0·75	2·92	4·195
VI.	1·15	67·315	0·13	—	20·815	2·885	1·66	—	2·025	trace.	0·595	3·37
								sulphur.				
VII.	3·125	40·21	0·15	0·66	24·01	4·21	11·27	trace.	4·105	6·52	1·67	3·53
VIII.	11·09	32·98	trace.	trace.	16·73	7·025	13·71	trace.	4·90	11·52	0·73	0·625
X.	4·61	58·30	0·23	trace.	21·89	7·055	2·57	—	0·305	1·095	2·45	1·135
								Mn_3O_4.				
X.	0·80	47·56	trace.	0·11	17·16	13·06	9·39	trace.	4·11	trace.	2·30	5·45
XI.	1·00	47·505	trace.	trace.	17·00	11·75	10·71	0·41	6·285	trace.	2·89	2·545
								Cr_2O_3				
XII.	10·56	38·70	trace.	trace.	17·59	15·04	4·56	0·14	4·98	6·00	trace.	0·845
XIII.	15·52	38·72	—	—	2·995	1·905	5·07 and 0·29 NiO	0·08	trace.	31·565	0·325	0·765
XIV.	0·665	65·165	—	—	19·08	0·50	—	—	1·625	trace.	10·37	2·40

X likewise contains traces of sulphur; XII and XIII, traces of an oxide of manganese.

In the estimation of silica in the foregoing analyses the following method was adopted. The fused mixture after treatment with hydrochloric acid was evaporated to dryness and *silica* (*a*) removed in the usual manner. The filtrate was evaporated to dryness and a small additional quantity of *silica* (*b*) separated. From this filtrate iron and

aluminium were precipitated as basic acetates, and collected. This precipitate was dissolved in hydrochloric acid, a few drops of nitric acid were added, and, after cooling, the bases were reprecipitated by ammonia, washed, dried, ignited, and weighed. This precipitate was dissolved in hydrochloric acid, and a third portion of *silica* (*c*) obtained by filtration. W. F.

"*New Mineral*" *from Burmah.** By D. WALDIE.

THE author publishes the results of an analysis of a "mineral," the physical characters of which he failed to notice, and the locality of whose occurrence in Burmah he did not determine. The percentage numbers are—

Copper	17·000
Silver	0·096
Iron	36·470
Antimony	1·150
Arsenic	32·700
Sulphur	1·360
Earthy matter	0·560
	89·336

The deficiency of over ten and a half per cent. is supposed to arise from loss of arsenic during the analysis. The silver is equal to $31\frac{1}{3}$ ounces troy to the ton.

A second sample subsequently received from the same source has a laminated structure and uneven fracture, is somewhat cellular and of a steel-grey colour with a purplish tint and metallic lustre; it is rather redder than mispickel. Minute specks of brownish-green matter were occasionally seen, particularly near the lamellæ. It gives no streak on paper, a dark-grey one on porcelain, has a hardness = 5·5, and a sp. gr. from 7·3 to 7·4. Its composition is:—

Soluble in hydrochloric acid:—

Copper oxide	1·21	
Iron protoxide	1·97	
Lead oxide	1·89	
Arsenious acid	1·12	
		6·19

Insoluble in hydrochloric acid:

Copper	12·13	
Iron	42·12	
Arsenic	38·45	
Antimony	0·54	
Earthy matter	0·12	
		93·36
		99·55

* Chemical News, xxiii, 4.

The constituents approximate to two equivalents of arsenic, six of iron, and one of copper. The author named this substance O'Rileyite.

W. F.

Supposed Native Copper. By H. Bowman.*

The specimen was found in a cargo of copper pyrites from the Tharsis mines in Spain. It weighed 21½ lbs., and has a sp. gr. of 8·4. The colour varies in different parts from copper-red to almost white, with a hackly fracture. The interior is full of cavities above shot size; the outer surface has no adherent matrix. Its composition is:—

Copper	84·80
Iron	5·54
Zinc	trace
Nickel	0·28
Cobalt	0·14
Antimony	0·50
Arsenic	7·10
Sulphur	0·73
Oxygen	0·41
	99·50

In three samples the percentages of iron were 4·8, 5·4, and 8·1.

Zircons.—A. H. Church† examined some rounded pebbles, each weighing about 2 grs., which came from Mudgee, New South Wales, and identified them as zircons. The specific gravity of the Mudgee stones was 4·704. They resembled the stones obtained from Expailly, in Auvergne.

W. V.

Gahnite, from Mine Hill, Franklin Furnace, New Jersey. By G. J. Brush.‡

The Mine Hill mineral differs from the gahnite of other localities in the frequent occurrence of the cubic plane. These planes are often the largest, giving the crystals the form of cubes with truncated dodecahedral edges, and only small octohedral planes. There are also minute planes of the trapezohedron 2–2, truncating the edges of the dodecahedron; others of the trigonal-trisoctahedron 3; and sometimes

* Chemical News, xxiii, 19.

† Chem. News, xxiii, 78.

‡ Amer. Journal of Science [3], i, 28.

two planes between the cubic and octahedral which appear to belong to the forms 4–4 and 8–8. These surfaces, rounded and feebly lustrous, blend in a curved surface, and do not admit of accurate measurement. The inclinations on a cubic plane are for 4–4, 160° 30′; for 8–8, 170° 30′. The crystals vary in diameter from $\frac{1}{8}$th to $1\frac{1}{2}$ inch, are blackish green, their fragments being olive-green, and have a hardness = 7·5, and a specific gravity = 4·89 – 4·91. Two analyses gave as a mean result:—

		Oxygen ratios.	
Alumina	49·78	23·20	25·77
Ferric oxide	8·58	2·57	
Zinc oxide	39·62	7·82	8·12
Manganous oxide	1·13	0·25	
Magnesia	0·13	0·05	
Silica	0·57	—	
	99·81		

This gives the ratio of oxygen of $\dot{R}$ and $\dddot{R}$ as 1 : 3·17. By assuming 1·56 per cent. of the ferric oxide to be present as the lower oxide, the ratio is exactly 1 to 3. This variety of gahnite is richer in zinc than any heretofore examined. It occurs in association with black mica, apatite, calcite, and a brownish variety of chrysolite which contains zinc.

W. F.

On the Mineral Constituents of Meteorites. By N. Story-Maskelyne.*

The *Breitenbach meteorite.*—This meteorite, found at Breitenbach in Bohemia, bears a great resemblance to the siderolite of Rittersgrün, in Saxony. It is a spongy metallic mass, the hollows of the iron being filled by a mixture of crystalline minerals. These are: a bronzite with the formula, $Mg\frac{4}{5}\,Fe\frac{1}{5}SiO_3$, orthorhombic in its crystalline form. The crystallography of this mineral was investigated by von Lang, and has been published in Pogg. Ann. cxxxix, 315. Secondly, a mineral composed of silica, having the specific gravity of quartz after fusion, and crystallised in the orthorhombic system.

The elements of the crystal are—

$$a : b : c = 1·7437 : 1 : 3·3120,$$

and the angles—

$$100 : 101 = 27° 46′$$
$$100 : 110 = 60° 10′$$
$$110 : 101 = 63° 19′$$

* Proc. Roy. Society, xix, 266.

The optic axes lie in a plane parallel to the plane 0·10, the first mean line being the normal to the plane 100. They are widely separated, and present in air an apparent angle of 107°. This mineral is beyond question orthorhombic, and as the tridymite of von Rath is hexagonal in its symmetry, the mineral of the Breitenbach siderolite will be a trimorphic form of silica. Its specific gravity was found to be 2·245, that of tridymite being 2·295 to 2·3, and that of quartz, 2·65. The analysis of the mineral, by distillation of the silica as silicic fluoride, and subsequent determination as potassium fluosilicate, gave 97·43 per cent. of silica, the remainder being oxide of iron and lime. A second analysis gave 99·21 per cent. silica, and 0·79 residue. The nickeliferous iron, the chief constituent of this meteorite, is an alloy of the formula $Fe_{10}Ni$, and contains a trace of copper. In addition to the above minerals, the iron encloses occasional well developed octahedrons of chromite, troilite, and a small amount of schreibersite.

The Shalka Meteorite.—Haidinger held this stone to be made up of a mineral which he termed piddingtonite, and which, according to von Hauer, might be a compound of bisilicate and trisilicate of iron and magnesium. The latter acid silicate, however, no more forms a constituent of this meteorite than does the other acid silicate, shepardite, as Dr. Laurence Smith has shown, enter into the composition of the Bishopsville meteorite. Haidinger's view that the Shalka stone, though apparently made up of two silicates, a grey and a mottled variety, is nevertheless composed of a single mineral species varying in colour, is now confirmed by analysis. It is found to be a bronzite of the formula $Mg^{\frac{2}{3}}Fe^{\frac{1}{3}}SiO_3$; in association with it are distinct crystals of chromite. Rammelsberg, who has recently published the results of his examination of this meteorite in Pogg. Ann. cxlii, 275, finds in it a bronzite associated with 12 per cent. of olivine. It is probable that the meteorite varies in composition in different parts, and that Rammelsberg analysed that portion in which an olivinous ingredient occurred in appreciable preponderance. On treating the mottled variety with hydrochloric and sulphuric acids, it was noticed that the action was in each case confined to that of a solvent.

W. F.

Organic Chemistry.

On Pyrene. By C. Graebe.*

Liebermann and the author described some time ago a mixture of solid hydrocarbons derived from coal-tar, and having a higher boiling point than anthracene. From this mixture a hydro-

* Zeitschr. f. Chem. [2], vii, 22, from Deut. Chem. Ges. Ber., iii, 738.

carbon, ascertained by Liebermann to be chrysene, $C_{18}H_{12}$, can be separated by sulphide of carbon, in which it is nearly insoluble. From the soluble portion the author has separated a hydrocarbon, $C_{16}H_{10}$, which he calls *pyrene*. The sulphide of carbon having been distilled off, the residue is repeatedly treated with boiling alcohol, used each time in quantity insufficient to dissolve the whole mass. In this way several crystallisations of hydrocarbons are obtained, the melting point of which varies between 80° and 160°. After several crystallisations from alcohol, they are dissolved in boiling alcohol, and treated with their own weight of picric acid in the same solvent. A quantity of *red* crystals at once separates, which increases as the liquid cools. This is crystallised from alcohol until the melting point of the hydrocarbon becomes constant. The picric acid compound is then decomposed by ammonia, whereby the pyrene is separated. It crystallises from alcohol in plates, dissolves slightly in cold alcohol, pretty freely in hot alcohol, and very easily in benzol, ether, and sulphide of carbon. It fuses at 142°, and, like anthracene, distils at a high temperature. Its red crystalline compound with picric acid is very distinctive, and is the only compound of a hydrocarbon with picric acid, besides the corresponding one of naphthalene, which is formed immediately on mixing together the alcoholic solutions, saturated at the ordinary temperature, of its two constituents. It is more stable than the anthracene compound. Pyrene is readily acted on by nitric acid, even of sp. gr. 1·2, diluted with six times its volume of water, being converted into nitropyrene. In solution in glacial acetic acid, pyrene is but very slightly attacked when boiled with chromic acid. Heated with a mixture of potassium chromate and sulphuric acid diluted with an equal bulk of water, it is converted into *pyrene-quinone*. With bromine it yields two different derivatives, accordingly as it is acted on in the dry state or in solution in sulphide of carbon, in the first case giving *dibromopyrene dibromide*, and in the second *tribromopyrene*. Heated with hydriodic acid to 180°—200° in sealed tubes, pyrene takes up hydrogen, becoming $C_{16}H_{12}$ and $C_{16}H_{14}$. Concentrated sulphuric acid heated with pyrene converts it into a sulpho-acid. *Pyrene-quinone* $C_{16}H_8(O_2)''$, is obtained as a red powder, slightly soluble in alcohol, ether, benzol, and sulphide of carbon, pretty freely in hot acetic acid, and very soluble in nitrobenzol. It sublimes in red needles, but most of it is decomposed. It resembles chrysoquinone in appearance, but is turned brown instead of blue by cold sulphuric acid. Powdered zinc reduces it to pyrene again; boiled with powdered zinc and dilute potash, it dissolves with red colour and separates again on exposure to the air. Pyrene is different from Glaser's diacetenylphenyl, $C_6H_5.C \equiv C - C \equiv C.C_6H_5$.

E. D.

On Tetraphenyl-ethylene, a Derivative of Benzone. By ARNO BEHR.*

THE author prepares benzone by distilling dry calcium benzoate, *without addition of lime*, and in this way obtains 40 per cent. of the theoretical amount. When benzone is heated to 180° in a sealed tube for 12 to 18 hours with excess of phosphorus pentachloride a chlorinated compound is formed, in which the oxygen of the benzone is displaced by two atoms of chlorine:

$$(C_6H_5)_2CO + PCl_5 = (C_6H_5)_2CCl_2 + PCl_3O.$$

On attempting to distil the yellow liquid thus formed, it is found that as soon as the phosphorus oxychloride has passed over, the liquid begins to turn brown and evolve hydrochloric acid. The temperature rises rapidly to near the boiling-point of benzone, whilst only a small quantity of chorinated oil distils, and the contents of the retort become brown and pasty and carbonize when further heated. The author endeavoured to remove chlorides of phosphorus by means of water, but without success, and was therefore under the necessity of operating with a mixture of the chlorinated compound with benzone. The compound is extremely active, at once attacking alcoholic ammonia, dry ammonia, silver acetate dissolved in glacial acetic acid, and other substances. Finely divided silver, obtained by reducing the freshly precipitated chloride with zinc, completely deprives it of chlorine. The action requires to be moderated by cooling, so that the temperature shall not rise above 200°, as otherwise the compound is decomposed, and hydrochloric acid set free. On distilling the product from a retort of hard glass, benzone passes over first, followed at a very high temperature, by the hydrocarbon, which solidifies in the neck of the retort. It dissolves very sparingly in alcohol and ether, but easily in hot benzol, from which it is deposited in pointed crystals as the solution cools. It is purified by precipitating the saturated benzol solution with a large quantity of alcohol, and then forms a white crystalline powder. Analyses of the body agree with the formula $C_{26}H_{20}$. After having been melted together, it melts at 221° (uncorr.). By the action of bromine, it yields the compound $C_{26}H_{17}Br_5$, and forms substitution-compounds with concentrated sulphuric and fuming nitric acids. J. R.

On Dibromobenzene. By VICTOR MEYER.†

PURE crystallised dibromobenzene, methyl iodide, and sodium were found to act upon one another only after standing for some hours, and when the ice surrounding the flask had melted. The action then

* Zeitschr. f. Chem. [2], vii, 25.
† Zeitschr. f. Chem. [2], vii, 26.

proceeded quite quietly, a large quantity of hydrocarbons being formed, of which the greater portion boiled at 135–140°. This body, when oxidized with potassium chromate and sulphuric acid, yielded *terephthalic acid*, which was found on careful examination to contain no trace of isophthalic acid. Moreover, when a mixture of the hydrocarbons was oxidized completely by distilling off the portion unacted upon after every 8 or 10 hours' boiling, and oxidising afresh, the terephthalic acid formed in abundance was free from any trace of isophthalic acid. Hence the position of the bromine-atoms in crystallised dibromobenzene is 1 : 4.

On a Sulphotoluene derived from Bromosulphotoluene. By H. HUEBNER, and F. C. G. MUELLER.*

IN a former communication, the authors have described a sulphobromotoluolic acid, the salts of which crystallise most beautifully, and could therefore be obtained in a state of perfect purity. It was to be expected that by replacing the bromine with hydrogen, a chemically pure sulphotoluolic acid would be obtained.†

To effect this, sodium amalgam was added to an aqueous solution of the sodium salt. After six days all the bromine was present as sodium bromide, from which the sodium salt of the new acid could not be separated by crystallisation as, like all the other salts, it is very soluble in water and alcohol. To isolate the acid, the liquid was neutralized with sulphuric acid, concentrated by evaporation, and evaporated to dryness after separation of Glauber's salt; the residue was treated with phosphorus pentachloride; and the chloride of the sulpho-acid after being well washed, was heated with water in a sealed tube to 130° for some hours. The contents of the tube were then boiled down in a flask until the temperature rose to 110°, and thick fumes of hydrochloric acid escaped, and a strong current of air was then blown through, by which all the remaining hydrochloric acid was expelled. On cooling the sulpho-acid solidified to a brown crystalline mass.

The salts of this acid are very soluble in water and alcohol, whilst those of the brominated acid are much less soluble; it is remarkable that the corresponding salts in the two series contain the same amount of water of crystallisation. The following were prepared:—

$(C_6H_4.CH_3SO_3)_2Ba + 2$ aq. is an indistinctly crystalline powder.

$(C_6H_4.CH_3SO_3)_2Ca$ does not crystallise from an aqueous solution. When a concentrated alcoholic solution is heated, the salt separates in small shining plates, which dissolve again on cooling. $(C_6H_4.CH_3SO_3)_2Pb$

* Zeitschr. f. Chem. [2], vii, 14.

† On acting upon toluene with sulphuric acid, two isomeric sulpho-acids are always formed, the separation of which is difficult.—C. S.

+ 2 aq. crystallises from the aqueous solution in thin plates, which are grouped in rosettes. From a concentrated alcoholic solution, it is precipitated by addition of ether in small shining plates. From a solution in absolute alcohol, it crystallises in long needles. $C_6H_4.CH_3SO_3Na$ + $\frac{1}{2}$ aq. crystallises from absolute alcohol in large shining plates. $C_6H_4.CH_3SO_3K$ + $\frac{1}{2}$ aq. is less soluble in absolute alcohol than the other salts, and crystallises from this solution in brilliant plates, which resemble naphthalene, and when formed very slowly, are grouped together in beautiful rosettes.

By acting on this last salt with phosphorus pentachloride, the pure sulphochloride $C_6H_4.CH_3SO_2Cl$ was obtained, as a faint yellow, transparent liquid, having a penetrating smell. By treatment with tin and hydrochloric acid, it was converted into the corresponding sulphydrate $C_6H_4.CH_3SH$, a colourless and strongly refractive liquid, which has a powerful odour, and is very caustic, destroying the skin. It forms mercaptides with metals.

Toluene bisulphide $(C_6H_4.CH_3)_2S_2$, is obtained by boiling the sulphydrate for some days with dilute nitric acid. It is a yellowish oil, which boils with partial decomposition at about 150°.

By boiling the chloride with aqueous ammonia, the amide $C_6H_4.CH_3SO_2NH_2$ is produced. To isolate it, the liquid is evaporated to dryness, and the residue exhausted with ether. From the boiling aqueous solution, it separates in small feathery crystals; once it was obtained in large plates. It is very readily soluble in alcohol, ether, and aqueous ammonia. The pure compound melts at 90—91°.

The authors believe that their acid is identical with the so-called metasulpho-toluolic acid, which has been investigated by Barth, Engelhardt and Latschinoff, and by A. Wolkow. They hope to settle this question definitively by further researches. C. S.

On some Derivatives of Isobutylic Alcohol. By K. Reimer.*

The isobutylic alcohol employed by the author was prepared from fusel-oil by Kramer and Pinner's process, and boiled at 108°. The *butyl bromide* obtained from it by the action of bromine and phosphorus boiled at 87°—88°. The bromide, heated to 150° with alcoholic ammonia, yielded the three butylamines, which were difficult to separate. After approximate separation of the three bodies by fractional distillation, the portion having the lowest boiling-point, when mixed with ethyl-oxalate, yielded at once the crystalline and easily purified *dibutyloxamide*, $C_2O_2N(C_4H_9)_2NH_2$, from which *monobutylamine*, $C_4H_9.H_2N$, boiling at 62°—65° (70°, Wurtz), was obtained by boiling with potassium hydrate. The portion of the crude butyl-bases boiling between

* Zeitschr. f. Chem. [2], vii, 26, from Deut. Chem. Ges. Ber., iii, 756.

110° and 130° was digested for some days with ethyl oxalate, and thus yielded *ethyl-dibutyloxamate*, $C_2O_2.N(C_4H_9)_2.OC_2H_5$, which gave *dibutylamine*, $(C_4H_9)_2HN$, boiling at 120°—122°, when boiled with potassium hydrate. The fraction of the butyl-bases having the highest boiling-point was digested with butyl bromide, until the base liberated by soda-ley boiled between 177° and 180°. The product consisted almost entirely of *tributylamine* $(C_4H_9)_3N$. All these amines yield exceedingly beautiful platinum-salts. It is remarkable that all attempts to prepare a tetrabutylammonium-compound have failed. Tributylamine, heated with butyl bromide under pressure, yields tributylamine hydrobromate and butylene. *Butyl sulphocyanate*, $CS.NC_4H_9$, obtained from butylamine, boils at 161°—163°, and forms with ammonia a fine crystalline sulphuretted urea, $(CS)(C_4H_9)H_3N_2$, melting at 90°—91°. The isomeric sulphocyanate obtained by the action of butyl sulphate on potassium sulphocyanate, boils at 174°—176°. Butylamine is likewise formed on heating salts of butylsulphuric acid with ammonia:

$$2C_4H_9KSO_4 + 4H_3N = K_2SO_4 + (H_4N)_2SO_4 + 2C_4H_{11}N.$$

The yield, however, falls far short of the theoretical amount, and the reaction cannot be recommended for the preparation of butylamine.

J. R.

On some transformations of Phenol. By L. BARTH.*

PHENOL is easily attacked by fused caustic potash, hydrogen being abundantly evolved. The fusion has to be stopped as soon as the mass assumes the consistence of a syrup. It contains, now, besides non-attacked phenol, salicylic acid and oxybenzoic acid, a new compound $C_{12}H_{10}O_2$, which the author calls diphenol.

To isolate this body, the fused mass is dissolved in water, an excess of sulphuric acid is added, and the liquid is shaken up with ether, which dissolves all the products formed. The acids are removed by shaking the solution with aqueous ammonium carbonate, and after evaporating the ether, the residue is subjected to fractional distillation to separate the phenol from diphenol, which boils at 340°—350°. By dissolving it in a solution of sodium carbonate, again exhausting with ether, and distilling, it is obtained pure. It is a very viscous oily liquid, which, after standing for some time, deposits crystals. It has a faint aromatic odour; water dissolves a small quantity; the solution gives a blue coloration with ferric chloride. It is soluble in alcohol, ether, caustic potash, and less in ammonia. It is acted upon by nitric acid, sulphuric acid, and phosphorus pentachloride; the products thus formed were not obtained in the pure state.

* Zeitschr. f. Chem. [2], vii, 18, from Ann. Ch. Pharm., clvi, 9.

By heating it with caustic potash and methyl iodide in presence of alcohol to 120°—130°, *dianisol* $C_{14}H_{14}O_2$ was formed, which was extracted from the products of the reaction with ether. It is a rather mobile liquid, boiling between 310°—320°, and having an aromatic odour. On standing, a crystalline powder separates out from it, consisting of microscopic octohedrons, which melt at 146°. They have the same composition as dianisol, and are either the pure compound or an isomeride. The liquid dianisol gives with bromine an amorphous substitution-product, and with nitric acid an indistinctly crystalline nitro-compound; the crystallised dianisol yields also an amorphous bromine-compound, but the nitro-compound crystallises in densely interwoven needles.

The author in all his experiments recovered a little more than one-half of the phenol; of diphenol, he obtained 12—15 per cent., and of the acids scarcely 1 per cent. He has convinced himself, that all these products are really derived from phenol, and not from an admixture, by using the non-attacked phenol over and over again, and by employing pure phenol obtained by distilling oxybenzoic acid with caustic lime. The author believes that the constitution of diphenol is expressed by the formula $\left\{\begin{matrix} C_6H_4OH \\ C_6H_4OH \end{matrix}\right.$. Each molecule of phenol loses one atom of hydrogen, and the two monad groups thus formed combine with each other. The formation of the two isomeric acids he explains by assuming that a phenol-residue, C_6H_4OH, unites with COOH resulting from the more complete oxidation of another molecule of phenol. C. S.

On the Action of Phenol on Ammonia. By M. Berthelot.*

Berthelot, on putting the reaction $C_6H_6O + NH_3 = C_6H_7N + H_2O$ to the test, by heating phenol which was saturated with gaseous ammonia when in the fused state, to 280° for 24 hours, obtained but a mere trace of aniline, using a solution of chloride of lime as a test. Heating to 360° did not increase the quantity of aniline to any appreciable extent. Phenol heated for several hours to 360 with ammonium chloride, or iodide, gave no trace of aniline.

Conversely, aniline gave no trace of phenol when heated for 20 hours with 10 parts of water to 310°. W. H. D.

On Phenylic Ether and Diphenylene Oxide. By W. Hoffmeister.†

As already stated in a preliminary notice, a mixture of phenol and diazobenzene-sulphuric acid evolves nitrogen, even in the cold, and more freely when gently warmed, and a thick oily liquid is formed which contains a body having an aromatic odour. On treating the

* Ann. Ch. Pharm., clvii, 109.

† Zeitschr. f. Chem. [2], vii, 24, from Deut. Chem. Ges. Ber., iii, 747.

mixture with excess of soda-ley, and distilling the portion insoluble therein from a retort in a current of steam, there passes over a pale-yellow oil, which sinks in water, and when purified by repeated rectification, solidifies completely in a cooling mixture to a mass of colourless long needles. The analysis of this body agrees exactly with the composition of phenylic ether:

$$C_6H_5N_2HSO_4 + C_6H_5OH = (C_6H_5)_2O + SH_2O_4 + N_2.$$

Phenylic ether forms a colourless solid mass, having an agreeable aromatic odour. It melts at 28° and boils at 248°. The slightest admixture of a foreign compound prevents its solidifying. It is insoluble in water, but mixes with ether in all proportions. It is not affected by distillation with phosphorus pentachloride, but is attacked by a mixture of the pentachloride and oxychloride when heated to 220° in a sealed tube for 10 hours. On opening the tube, hydrochloric acid escapes, and on distillation there pass over first a large quantity of phosphorus trichloride, followed by the oxychloride added, and lastly at 260—280°, a colourless chlorinated oil. Monochlorobenzene is not formed in this reaction. Phenylic ether is not reduced when its vapour is passed over zinc-filings heated in a combustion-tube. It is not attacked by hydriodic acid when heated therewith to 250° for 10 hours, nor by prolonged heating with a mixture of chromic acid and glacial acetic acid.

Phenyloxide-disulphuric acid. Concentrated sulphuric acid does not act upon phenylic ether in the cold, but when warmed in the water-bath, gradually dissolves it, and on diluting the product with water, a perfectly clear solution is obtained. The barium-salt, prepared in the usual manner, crystallises from its solution in small warty masses; when purified by recrystallisation it has the composition $C_{12}H_8O(SO_3)_2Ba$. It dissolves easily in water, alcohol, and ether. The free acid was obtained by decomposing the lead-salt with hydrogen sulphide and concentrating, as a syrupy liquid, which after standing for some time in a desiccator, deposited tolerably large, hard, colourless deliquescent crystals, easily soluble in alcohol, but insoluble in ether.

Diphenylene Oxide.—The author further examined the phenylic ether described by Lesimple (*Ann. Ch. Pharm.* 138, 375). This body crystallises readily from alcohol in fine colourless laminæ, having an agreeable aromatic odour, and the composition $C_{12}H_8O$. These crystals agreed perfectly in external characters and in melting-point with the body described by Lesimple. The compound is not acted upon when its vapour is passed over red-hot zinc filings. It is attacked by phosphorus pentachloride at 220° in a sealed tube, a chlorinated body being formed which crystallises from alcohol and melts at 92°.

J. R.

On the Action of Sulphuric Acid on Organic Chlorides containing Oxygen. By A. Oppenheim.*

(1.) *Monochlorhydrin of Glycol*, $C_2H_4.OH.Cl$, behaves just like ethyl chloride, C_2H_5Cl, evolving hydrochloric acid and forming the acid, $C_2H_4.OH.SO_4H$, already obtained from glycol and sulphuric acid, and described under the name of sulphoglycollic acid by Maxwell Simpson. (2.) *Epichlorhydrin*, C_3H_5ClO, unites with sulphuric acid to form a thick oil, $CH_2OH.CHSO_4H.CH_2Cl$, much heat being produced; potash removes the sulphuric acid from it. (3.) *Benzoyl chloride* is acted on much more energetically by sulphuric acid than by water, hydrochloric acid escaping in torrents, without the mixture becoming sensibly warm. When an excess of sulphuric acid is used, the new compound crystallises out in prisms. As soon as it is brought in contact with water, much benzoic acid separates. The crystals placed on a porous tile in a vacuum become opaque, amorphous, and completely soluble in water, without separation of benzoic acid. By adding the sulphuric acid to an excess of benzoyl chloride, heating, and distilling off the excess in a current of carbonic acid, a fused, hard, hygroscopic mass remains, which, like the preceding product, is completely soluble in water, and consists of sulphobenzoic acid, which in this way can be easily obtained, and in large quantity. (4.) *Acetyl chloride* gives with sulphuric acid only hydrochloric and acetic acids. (5.) *Chlorophthalic acid* gives with two molecules of sulphuric acid, an oily body, which by distillation yields at 280° a rapidly solidifying crystalline mass, breaking up with water into sulphuric and phthalic acids. (6.) *Monochlor-* and *trichlor-acetic acids* may be boiled with sulphuric acid without suffering any change. E. D.

On the Acids obtained by the Oxidation of Fermentation Butylic Alcohol. By E. Erlenmeyer.†

The oxidising action exerted on fermentation butylic alcohol by potassium chromate and sulphuric acid, appears to take place in two stages. In one case, where heat was not applied, isobutyric acid was the result. By heating the mixture, the isobutyric acid can be made to break up completely into carbon dioxide and acetic acid. In a quantitative experiment, 98·4 parts CO_2 were obtained per 100 parts isobutyric acid; in another case 100·4 CO_2. The equation $C_4H_8O_2 + O_6 = 2CO_2 + 2H_2O + C_2H_4O_2$ requires 100 CO_2 per 100 parts isobutyric acid. Normal butyric acid, according to Veiel, does not yield acids of the series containing less carbon than itself.

W. H. D.

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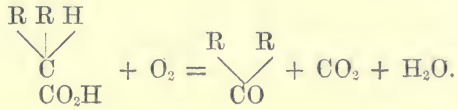
* Zeitschr. f. Chem. [2], vii, 21, from Deut. Chem. Ges. Ber., iii, 735.

† N. Repert. Pharm., xx, 86.

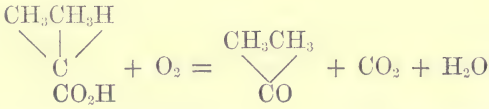
On the Oxidation of Isobutyric Acid. By A. POPOFF.*

THE observations of Chapman, Morkownikoff, and Buttlerow on the oxidation of some oxy-acids, and the hypotheses to which they have given rise, lead to the conclusion that in such oxidations the carbon atoms first attacked are those which are already partly combined with oxygen. For example—



Now there exist iso-acids (properly para-iso-acids) of the fatty series possessing a constitution exactly analogous to that of the oxy-acids, but containing hydrogen in the place of hydroxyl. It was to be expected that these bodies would behave towards oxidising agents in the same way as the oxy-acids. The correctness of this supposition has been confirmed by experiment in the case of *isobutyric acid.*

Isobutyric acid, prepared by Morkownikoff's process, is scarcely attacked by a mixture of potassium dichromate and dilute sulphuric acid, a very small quantity of carbon dioxide being formed after boiling for 24 hours. But when excess of isobutyric acid is heated to 140°—150° with an aqueous solution of chromic acid for 18 or 20 hours, a quantity of carbon dioxide escapes on opening the tube after cooling. On submitting the contents of the tube to distillation, and neutralising the distillate with potash, to remove free isobutyric acid and the acetic acid which might possibly be formed, an oily layer is obtained which boils at 55°—60° and possesses all the properties of *acetone.* Hence we have—



It is to be assumed, therefore, that all iso-acids of the above form yield by oxidation the corresponding ketones, the carbon-atom which is in combination with carboxyl, and with the smallest quantity of hydrogen, being first attacked.

J. R.

On the different Valeric Acids. By E. ERLENMEYER.†

IN connection with this subject, the author calls in question the value of the behaviour of a body towards polarised light, in determining

* Zeitschr. f. Chem. [2], vii, 4.

† N. Repert. Pharm., xx, 88.

chemical identity. He considers it possible that in liquids, as in solids, chemically identical molecules may act on polarised light when they are arranged in smaller or larger groups, but may produce no effect when they exist as single molecules. His experiments with different valeric acids may be thus summed up:—

(1.) Valeric acid from valerian root is optically inactive, and chemically identical with the acid from inactive amylic alcohol, and that from isobutyl cyanide. The three acids give the same barium salt, which is easily crystallisable.

(2.) The acid from active amyl alcohol, and that obtained by oxidising leucine (prepared from albuminous substances) are optically active, and have a somewhat higher specific gravity and lower boiling point than the inactive acid; their barium salt dries up to an amorphous glass.

(3.) The optically active acid, when heated with some drops of sulphuric acid to 200°, is converted, with partial carbonisation, into an acid which optically is quite inactive, but which possesses the other properties of the active acid, its barium salt also drying up to an amorphous glass.

From his experiments, Erlenmeyer infers that the active acid differs in constitution from the inactive acid; he thinks it will prove to be trimethyl-acetic acid or methyl-ethyl-acetic acid.

W. H. D.

On the action of Ammonia upon α-Chlorpropionic and β-Iodopropionic acid. By W. Heintz.*

When α-chlorpropionic acid is boiled with aqueous ammonia, a large quantity of *lactic acid* is formed, besides *alanine*. Alcoholic ammonia acts very slowly upon α-chlorpropionic acid; to accelerate the reaction, a little strong aqueous ammonia was added. Besides *alanine* and *ethyl-lactic acid*, a certain quantity of lactic acid was obtained, probably formed by the presence of the water.

Calcium ethyl-lactate, dried in the air, has the composition $(C_5H_9O_3)_2Ca + 2H_2O$; the salt, which was analysed by Wurtz, had been dried at 100°.

When α-chlorpropionic acid is heated with alcohol, α-chlorpropionic ether is formed, but no ethyl-lactic acid.

By treating β-iodopropionic acid with ammonia, an isomeride of alanine, which the author calls *ethylene-lactamic acid*, and *ethylene-dilactamic* (diparalactamic acid) are formed.† The latter compound corresponds to diglycollamic acid.

* Zeitschr. f. Chem. [2], vii, 19, from Ann. Ch. Pharm., clvi, 25.

† This compound would be better called *paralactamic*, or β-amidopropionic acid —C. S.

To effect the separation of the two acids, the solution was repeatedly boiled down with lead oxide, as long as ammonia was given off. On exhausting the residue with water, basic lead iodide was left behind; from the solution a lead salt of dilactamic acid was precipitated in colourless needles by addition of alcohol. This salt was dissolved in water, and converted into *acid dilactamate of lead*, by passing carbonic acid through the solution. This last salt crystallises from a hot alcoholic solution in very small and thin plates.

A better method of separation is to convert the two acids into the silver-salts. To effect this, the iodine and ammonia are removed as described, and the lead is precipitated from the solution by sulphuretted hydrogen. By adding silver-oxide to the filtrate, as long as silver dilactamide is formed—a salt which is almost insoluble in water—and passing sulphuretted hydrogen through the filtrate, a solution of ethylene-lactamic acid is obtained. This solution, when evaporated, leaves the acid as a syrupy liquid, which, by agitation with ether and repeated boiling of the residue with alcohol, is converted into a solid mass. The acid is readily soluble in water, but nearly insoluble in absolute alcohol. It crystallises in transparent prisms, belonging probably to the monoclinic system. On heating it to 170°, it turns brown, and sublimes very slowly in feathery needles; at a higher temperature it is completely decomposed, leaving a very difficultly combustible charcoal. It has a sweetish taste; the faint acid reaction of its concentrated solution is probably due to the presence of a little dilactamic acid. It combines with bases as well as with acids. The copper salt $(C_3H_6NO_2)_2Cu + 5H_2O$, which is much more soluble in water than the corresponding alanine compound, crystallises in large dark-blue rhombic prisms. With silver-nitrate the acid forms the compound $C_3H_7NO_2.AgNO_3$, in colourless needles, which deflagrate on heating.

Dilactamic acid, $C_6H_{11}NO_4$, which was obtained by decomposing the lead or silver-salt with sulphuretted hydrogen, remains on evaporation as a thick, colourless syrup gradually solidifying on standing to a radiate crystalline mass. Once by adding a particle of the solid acid to a concentrated solution, the author obtained distinct crystals, consisting of shining plates or flat needles. If, to the solution saturated with ammonia, silver-nitrate is added, a precipitate of *silver dilactamate* $C_6H_9NO_4Ag_2$ is obtained. On adding more silver-nitrate to the filtrate whilst warm, the compound $C_6H_{10}N_2O_7Ag_2 + 1\frac{1}{2}H_2O$ separates on cooling in colourless crystals. When ammonia is added to its solution, silver dilactamate is precipitated. The author did not succeed in obtaining corresponding lead and copper salts; neither was he able to prepare a crystallised nitrate of this acid.

By using alcoholic ammonia, the same compounds were formed as with aqueous ammonia. C. S.

On some Products obtained from Aspartic Acid. By EUGEN SCHAAL.*

INACTIVE aspartic acid has been obtained artificially from the ammonium salts of malic, maleïc, and fumaric acids; but this acid has not yet been transformed into asparagine. To effect this, the author prepared the acid silver salt of aspartic acid (which be obtained from asparagine), and heated it gently in the water-bath with ethyl iodide and a little alcohol. A reaction set rapidly in, iodide of silver and monethyl aspartate being formed. The latter compound is a crystalline substance which, after evaporating the alcohol and excess of ethyl iodide, was dissolved out with ether.

When this monethyl compound $C_2H_3\left\{\begin{matrix}COOH\\NH_2\\COOC_2H_5\end{matrix}\right.$, is treated with strong aqueous ammonia, it is easily converted into asparagine, possessing all the properties of the natural product.

When dry hydrochloric acid gas is passed over asparagine for three days, and the temperature is gradually raised to 180°, a white hard mass is formed. The same product is obtained by boiling asparagine with strong hydrochloric acid and heating the dried mass in a current of carbon dioxide, first to 120° and afterwards to 200°.

The body thus obtained is a mixture of two compounds; one which is sparingly soluble in cold water, can be extracted by boiling water; it has the composition $C_{16}H_{11}N_4O_9$, and is formed according to the equation—

$$4C_4H_7NO_4 = C_{16}H_{11}N_4O_9 + 7H_2O.$$

The residue, insoluble in water, is $C_{32}H_{26}N_8O_{17}$, formed according to the equation—

$$8C_4H_7NO_4 = C_{32}H_{26}N_8O_{17} + 15H_2O.$$

Both the soluble and the insoluble compound take up water when boiled with ammonia or baryta-water, and are converted into *inactive* aspartic acid.

C. S.

On the Sulpho-acids of Orthobromotoluene. By E. WROBLEVSKY.†

IT was shown in a former paper (*Zeitschr.* vi, 329) that, in the action of bromine on orthobromotoluene, the substituted bromine does *not*

* Ann. Ch. Pharm., clvii, 24.

† Zeitschr. f. Chem. [2], vii, 6.

occupy the para-position, and it became of interest to ascertain which position would be occupied by other bodies in orthobromotoluene. With this object the author has investigated its behaviour with fuming sulphuric acid.

The fuming acid must be added gradually to the bromotoluene, the mixture being kept cool at first and the combination finally aided by warming in a water-bath. On saturating the product with baryta, *three* barium salts (α, β, γ), separable with tolerable facility by fractional crystallisation, are obtained. The β-salt is most abundant, the α-salt less so (about 25 per cent.), while the proportion of γ-salt is very small (3 per cent.).

The *α-barium-salt* $(C_7H_6BrSO_3)_2Ba + H_2O$, crystallises in small prisms. 1,000 parts of water at 19° dissolve 5·28 parts of the salt. The *α-potassium-salt* crystallises in fine prisms. When melted with potassium hydrate it evolves a large quantity of hydrogen: the fused mass readily yields a considerable quantity of *salicylic acid*, melting at 155°. Hence this acid is *orthobromotoluene-metasulphuric acid.*

The *barium-salt of the β-acid*, $(C_7H_6BrSO_3)_2Ba + 3H_2O$, crystallises in fine shining laminæ. 1,000 parts of water at 190° dissolve 14·52 parts of the salt. The *β-lead-salt*, $(C_7H_6BrSO_3)_2Pb + 3H_2O$, and the *$\beta$-calcium-salt*, $(C_7H_6BrSO_3)_2Ca + 5H_2O$, form large prismatic crystals. The *β-potassium-salt* crystallises in large shining laminæ. When fused with potassium hydrate, this salt likewise yields a considerable quantity of *salicylic acid*; consequently this acid is also an *orthobromotoluene-metasulphuric acid.*

The *barium salt of the γ-acid*, $(C_7H_6BrSO_3)_2Ba + 5H_2O$, crystallises in needles. 1,000 parts of water at 19° dissolve 32·48 parts of the salt. As this acid is formed in very small proportion only, but little of it could be converted into potassium-salt and fused with potassium hydrate. The very small quantity of oxy-acid thus obtained did *not* colour ferric chloride, and was therefore oxybenzoic or paraoxybenzoic acid.

A *nitro-compound of β-orthobromotoluene-metasulphuric acid* is readily obtained by the action of nitric acid on the β-acid. *One* nitro-acid only appears to be formed. The *barium-salt*, $[C_7H_5Br(NO_2)SO_3]_2Ba + 7H_2O$, crystallises in needles, soluble in water. The *lead-salt*, $[C_7H_5Br(NO_2)SO_3]_2Pb + 3H_2O$, forms fine prismatic crystals, easily soluble in boiling water. The *calcium-salt*, $[C_7H_5Br(NO_2)SO_3]_2Ca + 9H_2O$, crystallises from alcohol in large prisms, very easily soluble in alcohol and water.

J. R.

On Sulphobenzoic Acid. By ADOR and OPPENHEIM.*

THE authors point out that the barium salt of the sulphobenzoic acid, described by Carius and Kämmerer (Ann. Ch. Pharm. cxxxi, 153), readily shows supersaturation, and does not differ in solubility from the salt previously investigated by Fehling. The sulphobenzoic acid from benzoyl chloride and sulphuric acid gives, like the ordinary sulphobenzoic acid, when fused with sodium formate, isophthalic acid (melting point 275°), and with potash, oxybenzoic acid (melting point 182°).

W. H. D.

On Sulphomaleic Acid. By R. MESSEL.†

FUMARIC acid combines directly with neutral potassium sulphite, forming the potassium salt of *sulphofumaric* acid (B. Credner),‡ and according to Messel, its isomeride, maleic acid, behaves similarly. On heating maleic acid for some hours with a solution of potassium sulphite in a retort connected with an upright condenser, and then allowing the liquid to stand, large colourless crystals were obtained, which gave on analysis numbers agreeing with the formula $C_4H_4K_2SO_7 + 2$ aq. The neutral potassium salt $C_4H_3K_3SO_7 +$ aq. is prepared by neutralising a solution of the above salt with potassium carbonate. On adding lead acetate to a solution of the acid salt, a yellowish-white, heavy precipitate is thrown down, which becomes crystalline on boiling. On decomposing this with hydrogen sulphide, an acid potassium salt of the formula $C_4H_5KSO_7$ is obtained. The neutral lead-salt may be prepared from this last-named salt by precipitation with lead acetate. On the addition of a barium salt to a solution of any of the above, the neutral barium salt is precipitated as a white powder. By the action of calcium carbonate on sulphomaleic acid, a non-crystalline calcium salt, probably of the composition $C_4H_4CaSO_7$ is obtained, and this, by neutralization with calcium hydrate yields the neutral salt. The silver salt $C_4H_3Ag_3SO_7$ is prepared from the acid potassium salt containing only 1 at. potassium, by neutralizing with ammonia and precipitating with silver-nitrate; it is a heavy precipitate, slightly soluble in cold, readily soluble in hot water. The free acid is obtained by decomposing the silver-salt with hydrogen sulphide. On heating sulphomaleic acid or its salts to fusion with potassium hydrate, it is decomposed into *fumaric* acid and sulphite. Messel has also examined, for the purpose of comparison, the barium, calcium, and silver-salts of *sulphosuccinic* acid prepared by Fehling's method, and finds them in all respects identical with those of sulpho-

* Zeitschr. f. Chem. [2], vii, 22, from Deut. Chem. Ges. Ber., 1870, 738.

† Ann. Ch. Pharm., clvii, 15.

‡ Inaugural-Dissertation; Tübingen, 1869.

maleic acid. Sulphosuccinic acid also yields fumaric acid, on fusion with potassium hydrate, but this is, perhaps, not a primary product of decomposition, but results from the malic acid first formed. From the absolute identity of the silver-salts he concludes that the three acids, sulphofumaric, sulphomaleic, and sulphosuccinic are identical, and not isomeric, and are represented by the constitutional formula, $COOH—CH_2—CHSO_2OH—COOH$.

H. E. A.

On Sulpho-pyrotartaric Acid. By THEODOR WIELAND.*

THE author says: it appears that the non-saturated carbon-compounds, in which two carbon atoms are connected by two combining powers,† unite directly with the alkaline *bisulphites*. He investigated the sulpho-acids obtained by this reaction from the three isomeric bodies, *itaconic*, *mesaconic*, and *citraconic acids*.

The result of this somewhat incomplete research is, that the three isomeric acids yield one and the same sulpho-acid, $C_3H_5\left\{\begin{matrix}CO.OH\\SO_3H\\CO.OH\end{matrix}\right.$, which he calls *sulpho-pyrotartaric acid*, as he does not doubt that the same body will be obtained by the action of fuming sulphuric acid upon pyrotartaric acid.

To prepare the acid, he boiled a moderately concentrated solution containing one of these acids and *neutral* potassium sulphite, in a retort connected with a reversed condenser for four to five hours. The potassium-salt of the new acid thus obtained is an amorphous mass. The barium- and lead-salts are slimy precipitates, which are most difficult to wash.

The only salt which was obtained in a pure state and analysed, was the calcium-salt, a crystalline precipitate obtained by adding calcium chloride to a solution of the potassium-salt; it is moderately soluble in boiling water, and can easily be obtained pure by recrystallisation. Dried in the air, it has the composition $(C_5H_{10}S_2O_7)_2Ca_3 + 7H_2O$; at 100° the salt loses 5 molecules of water, another at 160°, and the last at 180°; above 190° it begins to decompose.

To obtain the free acid from this salt, oxalic acid cannot be used, as it does not produce complete decomposition; it was therefore treated with sulphuric acid and dilute alcohol. On evaporating the alcoholic

* Ann. Ch. Pharm., clvii, 34.

† The term non-saturated implies that these compounds contain carbon-atoms with free combining powers. Most chemists, however, are now of opinion that in these compounds, two carbon-atoms are linked together by more than one unit of combining capacity. Kekulé calls such bodies "Wasserstoffärmere Verbindungen." It would be desirable to have an equivalent English term.—C. S.

solution, the acid remained in indistinct crystals. It is very soluble in water; the small quantity produced prevented the author from obtaining it free from sulphuric acid and the acid calcium salt. The acid potassium and ammonium salts form warty crystals, readily soluble in water. The neutral potassium salt is not precipitated by iron, copper, mercury, or zinc salts.

On boiling the potassium salt with a little water and an excess of caustic potash down to a crumbling mass, potassium sulphite and the potassium salt of a new acid are formed by replacement of the monad group, SO_3H, by hydroxyl. To obtain the free acid, the fused mass was decomposed by dilute sulphuric acid; the solution concentrated by evaporation, and the residue shaken with alcohol; the alcoholic solution boiled down; the residue treated with barium carbonate; and the barium salt thus obtained, which is very soluble in water, was decomposed by sulphuric acid.

The acid forms small, hard crystals, readily soluble in water, sparingly in alcohol and ether. The silver-salt contains 59·5 per cent. of silver, which agrees with the formula $C_3H_5\left\{\begin{matrix}COOAg\\OH\\COOAg\end{matrix}\right.$.

The acid has the composition and all the properties of *oxypyrotartaric acid*, which Maxwell Simpson obtained by the action of caustic potash upon dicyanhydrin, $C_3H_5\left\{\begin{matrix}CN\\OH.\\CN\end{matrix}\right.$ The author leaves it, however, undecided whether those two bodies are identical or not, as he did not determine the melting-point of his acid. Simpson's acid melts at 133°. C. S.

Action of Bromine on Acetic Aldehyde. By W. HAARMANN.*

BY the regulated action of bromine on aldehyde, a compound is formed which crystallises in long needles, soluble in ether, alcohol, and water. This body possesses a penetrating, tear-exciting odour, and exhibits the composition of dibromaldehyde, $C_2H_2Br_2O$. It instantly reduces silver-nitrate to the metallic state. The above formula is further supported by the fact that, under slightly altered conditions, bromine acting on aldehyde produces dibromacetic acid.

J. R.

Action of Cyanic Acid on Acrolein. By F. MELMS.†

ACROLEIN absorbs cyanic acid with avidity, the same phenomena being observed as in the corresponding experiment with acetic aldehyde. On

* Zeitschr. f. Chem. [2], vii, 27, from Deut. Chem. Ges. Ber., iii, 758.

† Zeitschr. f. Chem. [2], vii, 27, from Deut. Chem. Ges. Ber., iii, 759.

treating the product of the action with hot hydrochloric acid, the trigenic acid of the allyl series crystallises from the liquid, as it cools, in colourless needles, which dissolve with some difficulty in water. The ammonium-salt of the acid gives a white amorphous precipitate with silver-nitrate.

J. R.

Conversion of Chloral into Aldehyde by inverse Substitution. By J. PERSONNE.*

THE author obtained aldehyde by adding zinc to a solution of chloral hydrate acidulated with hydrochloric or sulphuric acid. In an experiment, in which the action was moderated by adding the acid gradually and in small quantities only, to the zinc and chloral, sufficient aldehyde was obtained to prepare the ammonia compound, and render its identity certain. At the same time, polymers of aldehyde are formed, in particular paraldehyde.

By passing ammonia gas into a well cooled vessel containing small quantities of anhydrous chloral, trichloraldehyde-ammonia, $C_2HCl_3O.NH_3$ is obtained, very similar in its properties to aldehyde-ammonia. When ammonia is passed, not so slowly, into quantities of chloral greater than 2 or 3 grms., the liquid, even when well cooled, becomes heated, and besides the trichloraldehyde-ammonia, chloroform, and formamide, CH_3NO, are produced, owing to secondary reaction, thus: $C_2HCl_3O + NH_3 = CHCl_3 + CH_3NO$.

W. H. D.

The Quality of Chloral Hydrate. By B. H. PAUL.†

THIS paper contains the results of an examination of several commercial preparations of chloral. Twelve samples from various sources, representing the chloral hydrate now supplied in the market, were analysed by heating with ammonia in tubes, to about 40° C. for three or four hours. The volume of the chloroform produced by the action of the alkali is measured, and the percentage by weight obtained by calculation, 1·497 being taken as the sp. gr. of chloroform. The following are the results obtained:—

* Ann. Ch. Pharm., clvii, 113.

† Pharm. Journ. Trans. [3], i, 621.

No. of Sample.	Characters.	Percentage chloroform obtained by weight.
1	White amorphous dry lumps	69·10
2	Hard transparent fragments of crystals	71·86
3	Thin translucent crystalline cake	71·86
4	White opaque cake, apparently not quite dry, especially at one surface	62·87
5	Very small crystals, aggregated into translucent lumps, with a slightly moist appearance	70·36
6	White semitranslucent cake, with slightly moist appearance	71·86
7	Translucent crystalline cake, consisting of small scaly crystals, moist and greasy to the touch	71·10
8	Large tabular crystals, like chlorate of potash	64·86
9	Translucent lumps, consisting of scaly crystals, slightly moist to the touch	67·36
10	Small acicular crystals, apparently breaking up into scales when rubbed in the hand, slightly moist to the touch	70·30
11	White opaque lumps, resembling effloresced carbonate of ammonia, with distinct crystalline fracture, translucent at the interior, and greasy to the touch	69·40
12	Chloral alcoholate	56·13
	Pure chloral alcoholate	61·76
	Pure chloral hydrate	72·20

Two other samples, examined by Dr. Versmann, had the following properties:—

Samples.	Physical properties.	Percentage of chloroform, by weight.	Corresponding percentage of pure chloral hydrate.
Crystals	Boiling point = 96° to 97° C.	70·3	97·4
	Point of re-solidification = 49° C.	..	..
Cake	Sp. gr. at 49° C. = 1·61	69·4	96·2

Both samples are pure chloral hydrate, which have by exposure attracted some moisture. The absence of alcohol was proved by the non-formation of iodoform, after decomposition by ammonia and separation of chloroform.

Dr. Paul regards as the purest form of chloral hydrate that which presents commonly the appearance of ordinary alum broken into fragments about the size of grains of paradise, the fragments being perfectly transparent, free from powder, only slightly odorous, dry to the hand, and not becoming moist by exposure. The definite needle-shaped crystals, like ammonium oxalate, sometimes met with, are, he believes, characteristic of the alcoholate. W. H. D.

Action of Chlorine on Hydrocyanic Acid in Alcoholic Solution. By C. BISCHOFF.*

THE author found that when chlorine acts upon mercuric cyanide, the compound $C_8H_{14}Cl_2N_2O_4$, as observed by Stenhouse, is invariably produced, but when an alcoholic solution of hydrocyanic acid is employed a compound having the formula $C_8H_{15}ClN_2O_4$ is formed in most cases. The properties of the new body closely resemble those of the compound already known. It crystallises in white silky needles, which are distinctly softer than the crystals of Stenhouse's body. Its melting point is 147°. The compound dissolves easily in ether and alcohol, and also in warm nitric acid, from which it is precipitated by water. It is insoluble in hydrochloric acid. Sulphuric acid dissolves it, with evolution of heat, forming a yellow solution. When this solution is heated, the compound is broken up, alcohol and carbon dioxide being eliminated, with simultaneous formation of ammonium sulphate and sulphur dioxide. Soda-ley and baryta-water likewise resolve the body into alcohol, carbon dioxide, and ammonia. When heated with hydrochloric acid in sealed tubes, it yields carbon dioxide, ethyl chloride, and ammonium chloride. All these decompositions are accompanied by partial carbonisation. By the action of alcoholic ammonia, a viscid yellowish-brown base is formed, which absorbs carbon dioxide from the air; its composition of which has not yet been determined.

J. R.

On a New Class of Cyanic Ethers. By A. W. HOFMANN.†

AN examination of the body obtained by the action of phosphorus-bases on phenyl cyanate has shown that it is not identical with either phenyl cyanurate or phenyl isocyanurate. The cyanurate obtained from triphenylmelamine melts at 260°; the isocyanurate derived from phenol melts at 224°; whilst the melting-point of the new compound is 175°. This body differs also in its other properties from the cyanurates previously known. Similar reactions to that occurring with phenyl cyanate take place under the same conditions with methyl and ethyl cyanates. Ethyl cyanate is converted, slowly at ordinary temperatures, more rapidly at the temperature of boiling water, under pressure, into a viscid liquid, which afterwards solidifies to a crystalline mass. Methyl cyanate, placed in contact with a drop of triethylphosphine, is instantly converted into a crystalline mass, with considerable evolution of heat. The body obtained from ethyl cyanate melts at 95°, and is probably identical with the ethyl cyanurate already

* Zeitschr. f. Chem. [2], vii, 27, from Deut. Chem. Ges. Ber., iii, 760.

† Zeitschr. f. Chem. [2], vii, 29, from Deut. Chem. Ges. Ber, iii, 765.

known. The melting point of ordinary methyl cyanurate is 175°; that of methyl isocyanurate is 132°; the new compound melts at 98°.

$$\left.\begin{matrix}CO\\C_6H_5\end{matrix}\right\}N \qquad \left.\begin{matrix}(CO)_2\\(C_6H_5)_2\end{matrix}\right\}N_2 \qquad \left.\begin{matrix}(CO)_3\\(C_6H_5)_3\end{matrix}\right\}N_3.$$

Phenyl cyanate. New compound. Phenyl cyanurate.

On a New Mode of forming Isonitriles. By A. W. HOFMANN.*

ALLYL sulphocyanate and 1 molecule of triethylphosphine yield, as is known, a urea containing both nitrogen and phosphorus. This body, when heated, is resolved into triethylphosphine sulphide and the isonitrile of the allyl series:

$$[CS.C_3H_5.(C_2H_5)_3]NP = (C_2H_5)_3PS + C_3H_5.CN.$$

The sulphocyanates of methyl, ethyl, and amyl behave in exactly the same manner. On mixing together the phosphorus-base and the sulphocyanate, a rise of temperature takes place, and the odour disappears, evidently owing to the formation of a compound analogous to the urea mentioned above. When the mixture is further heated under pressure, magnificent crystals of triethylphosphine sulphide are deposited on cooling, whilst at the same time the pungent odour of the isonitrile of the series reveals itself.

J. R.

On a reaction of Chloroform. By A. W. HOFMANN.†

To detect small quantities of chloroform, especially in presence of ethereal compounds closely allied to it, and possessing similar properties, advantage may be taken of its behaviour with the monamines in presence of alcohol and sodium hydrate. The odour of isonitriles thereby produced is an infallible sign of the presence of chloroform. The experiment is performed by adding the liquid to be tested to a mixture of aniline—any other primary monamine, fatty or aromatic, serves equally well—and alcoholic soda. If chloroform is present, a violent reaction takes place, either immediately or on warming gently, and the peculiar-smelling vapour of the isonitrile is evolved. Bromoform and iodoform, of course, behave like chloroform: the reaction occurs, moreover, with all bodies capable of yielding chloroform, bromoform, or iodoform by the action of alkalis. For example, on adding a solution of chloral in aniline to alcoholic potash, the

* Zeitschr. f. Chem. [2], vii, 29, from Deut. Chem. Ges. Ber., iii, 766.

† Zeitschr. f. Chem. [2], vii, 30, from Deut. Chem. Ges. Ber., iii, 769.

vapour of an isonitrile is immediately evolved in abundance. *Chlorethylidene*, treated with alcoholic potash and aniline, yields no isonitrile, and is therefore easily distinguished from chloroform. The reaction here recommended is so delicate, that one part of chloroform dissolved in 5000 to 6000 parts of alcohol may be detected with certainty.

On the Aromatic Cyanates. By A. W. HOFMANN.*

THE only member of this class which has hitherto been obtained, but only imperfectly studied, is phenylic cyanate. The author's researches on the mustard oils led him to a simple process for the preparation of this and other aromatic cyanates. In a former paper he drew attention to the facility with which the mustard-oils combine with a molecule of alcohol, forming half-sulphuretted urethanes, which, when distilled alone, or, better, with phosphoric anhydride, again split up into their components, thus—

$$\left.\begin{matrix}CS(C_6H_5)HN\\C_2H_5\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}CS\\C_6H_5\end{matrix}\right\}N.$$

Taking the results of these experiments into consideration, it was to be expected that phenylic cyanate would be formed on distilling phenyl-urethane with phosphoric anhydride.

Phenyl-urethanes or phenyl-carbamic ethers had already been obtained by treating the phenylic cyanate with methyl-, ethyl-, or amyl-alcohol, and since then ethyl-phenyl urethane has been carefully studied by Wilm and Wischin, who prepared it by acting upon aniline with chloro-carbonic ether:

$$CO\left\{\begin{matrix}C_2H_5\\Cl\end{matrix}\right. + 2(C_6H_5)H_2N = CO\left\{\begin{matrix}OC_2H_5\\N(C_6H_5)H\end{matrix}\right. + (C_6H_5)H_2N.HCl.$$

The author has repeated the experiments of these gentlemen, and confirms their results, with the exception of the statement that this ether volatilizes without decomposition; he finds that on distillation some of it always splits up into phenylic cyanate and alcohol:

$$\left.\begin{matrix}CO(C_6H_5)HN\\C_2H_5\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}CO\\C_6H_5\end{matrix}\right\}N.$$

This decomposition becomes complete if the urethane is heated with phosphoric anhydride; the alcohol remains behind, and pure phenylic

* Proc. Roy. Soc., xix, 108.

cyanate distils over as a colourless liquid, having a great refractive power, and boiling at 163° (not, as he formerly stated, at 178°). It has a very pungent smell, and its vapour excites a copious flow of tears. The behaviour of this body with other substances has already been described in the author's former papers. With water it yield. carbonic acid and diphenylguanidine; it combines with alcohol, the urethane being reproduced; and with ammonia and the compound ammonias it forms an inconceivable number of ureas. But the most characteristic reaction which it exhibits is, that on dipping a glass rod, moistened with triethyl phosphine, into a large quantity of the cyanate, it becomes very hot in a few moments, and solidifies to a mass of beautiful crystals, being transformed into a polymeric cyanurate.

Tolylurethane, $\left.\begin{matrix}CO(C_7H_7)HN\\C_2H_5\end{matrix}\right\}O$, is obtained by the action of chlorocarbonic ether upon toluidine; the reaction is so violent, that it is advisable to conduct it in presence of ether. When the solution filtered from the toluidine hydrochlorate is evaporated, it leaves the tolylurethane as an aromatic oil, which, when cooled by a freezing mixture, solidifies with difficulty. It is insoluble in water; from alcohol it crystallises in long prisms melting at 32°. On distilling it with phosphoric anhydride, *tolyl cyanate*, $\left.\begin{matrix}CO\\C_7H_7\end{matrix}\right\}N$, passes over, a colourless liquid, boiling at 185°, and showing in all its properties the greatest resemblance to the phenylic compound; triethylphosphine acts on it however more slowly.

The reaction of xylidine with chlorocarbonic ether is more sluggish than that with aniline; *xylylurethane*, $\left.\begin{matrix}CO(C_8H_9)HN\\C_2H_5\end{matrix}\right\}O$, crystallises in fine needles, which melt at 58°.

Xylyl Cyanate, $\left.\begin{matrix}CO\\C_8H_9\end{matrix}\right\}N$, is a colourless, highly refractive liquid, boiling at about 200°, and possessing only a feeble odour; it exhibits reactions similar to those of the other aromatic cyanates, but they often require days to be completed.

Naphthylurethane, $\left.\begin{matrix}CO(C_{10}H_7)HN\\C_2H_5\end{matrix}\right\}O$, obtained by treating naphthylamine with chlorocarbonic ether, crystallises from alcohol in needles, which melt at 79°.

Naphthyl cyanate, $\left.\begin{matrix}CO\\C_{20}H_7\end{matrix}\right\}N$, is a colourless, not very mobile liquid, boiling at about 269°–270°. At the ordinary temperature it is almost odourless, but its vapour has the pungent smell peculiar to the cyanic ethers. With water, alcohols, and ammonias it gives the characteristic reactions of that class of bodies, and acts with incomparably greater quickness and precision than the xylyl compound. This is particu-

larly shown in the action of triethylphosphine, which causes the cyanate of the naphthyl series to solidify almost instantaneously.

C. S.

On the Action of Acetic acid on Phenyl Sulphocyanate. By A. W. HOFMANN.*

WHEN a mixture of the two bodies is heated to 130°—140° for some hours, under pressure, carbon dioxide and hydrogen sulphide escape on opening the tube, and the liquid when poured out solidifies to a mass of splendid crystals, which are obtained in a state of perfect purity by recrystallising them once from alcohol. The body (phenyl-diacetamide) resembles acetanilide in its properties. It melts at 111° (?). When heated with alkalis, it yields, as might be expected, aniline and acetate:

$$CS.C_6H_5N + C_2H_3O.OH = CS(C_6H_5)HN.O(OC_2H_3O)\ (?);$$

and

$$CS.(C_6H_5)HN.O(OC_2H_3O) + C_2H_3O.OH = C_6H_5.(C_2H_3O)_2.N + CO_2 + H_2S.$$

J. R.

On a Reaction of Cyanuric Acid. By A. W. HOFMANN.†

CYANURIC acid, if present in the free state and in any considerable quantity, is most readily detected by heating the highly dried substance in a short narrow tube. The smell of the vapour of cyanic acid thereby evolved is so characteristic, that there is little room for doubt as to presence or absence of the acid. To detect the acid when in solution, however, and present in extremely small quantity only, advantage may be taken of the sparing solubility of sodium cyanurate in hot concentrated soda-ley. The liquid to be tested is placed in a watch-glass, mixed with strong soda-ley, and warmed for a moment over a pointed flame. If cyanuric acid is present, splendid delicate needles of the sodium-salt at once make their appearance, spreading from the point at which the flame is applied, and disappearing again as the liquid cools, provided the solution is not too strong. The formula of sodium cyanurate is $Na_3C_3N_3O_3$. J. R.

* Zeitschr. f. Chem. [2], vii, 31, from Deut. Chem. Ges. Ber., iii, 770.

† Zeitschr. f. Chem. [2], vii, 31, from Deut. Chem. Ges. Ber., iii, 769.

Diagnosis of Primary, Secondary, and Tertiary Amines. By A. W. HOFMANN.*

IT is a well-known fact that the *primary* amines alone are capable of yielding the isonitriles with chloroform and potash-ley. This reaction being of extraordinary delicacy, and the odour of the isonitriles being quite unmistakable, though it varies to some extent with different radicals, the presence of a primary amine may be distinguished without the slightest difficulty. It is only necessary to dissolve a few centigrammes of the base in alcohol, and mix the solution with alcoholic potash or soda in a test-tube, and, having added a few drops of chloroform, to warm gently. If a primary amine is present, a violent reaction occurs, and vapours of isonitrile, recognisable by their simultaneous effect upon the nose and the tongue, are at once evolved. If in this experiment the characteristic odour of isonitrile is not perceived, the question remains, whether the base under examination is a secondary or a tertiary amine. In this case the formation of sulphocyanates may be taken advantage of. It has been proved by experiment that both *primary* and *secondary* amines yield sulphocyanates, analogous to mustard-oil, the peculiar odour of which is easily recognisable. The experiment is made by dissolving a few centigrammes of the base in alcohol, mixing the solution with about an equal volume of carbon bisulphide, and evaporating a part of the alcohol. The residual liquid is then heated with an alcoholic solution of mercuric chloride. If a primary or secondary amine is present, the irritating odour of the sulphocyanate of the series is at once perceived. Unfortunately this reaction is not quite general. The first reaction described above is common to all primary amines, whether belonging to the fatty or to the aromatic series; but in the case of the secondary bases, the formation of sulphocyanates takes place only with amines of the fatty series, or with mixed amines. To distinguish between secondary and tertiary aromatic amines, which do not yield sulphocyanate, recourse must be had to the old method of treatment with methyl iodide, &c.

J. R.

On Ethylene-bases. By A. W. HOFMANN.†

A MIXTURE of ethylene bromide and alcoholic ammonia deposited, on standing for some months, considerable quantities of a white compound, which, when treated with water, was found to consist of a mixture of ammonium bromide with an amorphous body, nearly insoluble in

* Zeitschr. f. Chem. [2], vii, 29, from Deut. Chem. Ges. Ber., iii, 767.

† Zeitschr. f. Chem. [2], vii, 28, from Deut. Chem. Ges. Ber., iii, 762.

water, alcohol, and ether. This peculiar substance was shown by analysis to be a mixture of salts of *tetrethylene-triamine*, with 1, 2, and 3 molecules of hydrobromic acid $(C_2H_4)_4HN_3.HBr$, $(C_2H_4)_4HN_3.2HBr$, and $(C_2H_4)_4HN_3.3HBr$. On prolonged boiling with ammonia, the hydrobromic acid is removed, and corresponding hydrates, resembling the salts in being amorphous and uncrystallisable, are formed. From these hydrates the other salts of the bases may be obtained.

J. R.

On Aldehyde-green. By A. W. HOFMANN.*

CRUDE aldehyde-green in the pasty state still contains sodium sulphate and acetate. It is freed from these and all other mineral substances by washing with warm water, and then leaves no incombustible residue when burnt on platinum foil. Many attempts were made to crystallise the body thus purified, or to convert it into a crystalline compound, but without success. The washed green was therefore dissolved in alcohol, and the solution precipitated by ether, this process being repeated several times, to ensure as pure a product as possible. The fine green amorphous mass was found to contain sulphur. When dried in a vacuum it has the composition represented by the formula, $C_{27}H_{27}N_3S_2O$.

J. R.

On the Action of Cyanogen on Aniline. By A. W. HOFMANN.†

TOGETHER with aniline cyanide there is formed a red crystalline mass, which, when purified by suitable means, yields fine red crystals of a mono-acid base, having the formula $C_{21}H_{17}N_5$, and yielding with hydrochloric acid the crystalline salt $C_{21}H_{17}N_5.HCl$. This body may be regarded as a modified triphenyl-guanidine, and on this view may be represented by the formula $C[N_3.H_2(C_6H_5)_3].2CN$. When heated with weak spirit (best under pressure) the base is resolved into diphenyl-parabanic acid, with elimination of ammonia and analine:

$$C[N_3.H_2(C_6H_5)_3].2CN + 3H_2O = CO.C_2O_2.N_2(C_6H_5)_2 + 2H_3N + C_6H_7N.$$

On boiling the alcoholic solution of the base with concentrated hydrochloric acid for some time, the diphenylparabanic is also decomposed, and ultimately ammonia, aniline, carbon dioxide, and oxalic acid are produced.

* Zeitschr. f. Chem. [2], vii, 28, from Deut. Chem. Ges. Ber., iii, 763.

† Zeitschr. f. Chem. [2], vii, 28 from Deut. Chem. Ges. Ber., iii, 764.

Action of Cyanogen on Triphenylguanidine. By A. W. HOFMANN.*

AN alcoholic solution of triphenylguanidine absorbs large quantities of cyanogen; after standing some time the saturated solution deposits yellowish-white crystals, which may be purified by recrystallisation. This body has the same composition as that formed by the action of cyanogen on aniline, namely, $C_{21}H_{17}N_5$, but differs from it in colour, crystalline form, solubility, and more especially in its behaviour with acids. In contact with hydrochloric acid, it assumes a deep yellowish-red colour, evidently due to the formation of a salt, which, however, cannot be isolated, the red body being speedily resolved, with elimination of ammonia, into a crystalline yellow compound, which must be regarded as *oxalyltryphenylguanidin*, $C.C_2O_2.N_3(C_6H_5)_3$, formed according to the equation:

$$C_{21}H_{17}N_5 + 2H_2O = C_{21}H_{15}N_3O_2 + 2H_3N.$$

This compound, when boiled with alcohol and hydrochloric acid, yields aniline and diphenylparabanic acid, the latter body being ultimately resolved into aniline, oxalic acid, and carbon dioxide.

J. R.

Synthesis of Substituted Guanidines. By E. ERLENMEYER.†

THE author, in continuation of a previous experiment in which he obtained hydrochloride of guanidine by heating ammonium chloride in alcoholic solution with cyanamide, has obtained salts of phenyl-, tolyl-, and methyl-guanidine by the action of the hydrochlorides of phenylamine, toluidine, and methylamine on cyanamide.

The methylguanidine thus obtained does not appear to differ perceptibly in its own properties or those of its salts, from the description given of methyluramine, obtained by oxidising creatine or creatinine. The platino-chloride, however, said by Senarmont to crystallise in rhombohedrons, by Dessaignes, in flattened prisms, was obtained in hendyohedrons belonging to the monoclinic system. The author proposes to prepare methylguanidine by Dessaignes' method, and submit the two platino chlorides to H. v. Kobell for comparison.

W. H. D.

Synthesis of Alkaloids.‡

SCHIFF has succeeded in producing by synthesis a product which possesses the characteristic properties of the active principle of

* Zeitschr. f. Chem. [2], vii, 28, from Deut. Chem. Ges. Ber., iii, 761.

† N. Repert. Pharm., xx, 85.

‡ Pharm. J. Trans. [3], i, 605.

hemlock (*Conium maculatum*). When alcoholic ammonia acts upon butyraldehyde, at a temperature not above 100° C., two bases are produced, one of which, dibutyraldine, is represented by the following formula:

$$\underset{\text{Dibutyraldine.}}{C_8H_{17}NO} = \underset{\text{Butyraldehyde.}}{2C_4H_8O} + NH_3 - H_2O.$$

By the dry distillation of dibutyraldine, there is obtained amongst other products, a final one which has the composition of the alkaloid in question:

$$\underset{\text{Dibutyraldine.}}{C_8H_{17}NO} = H_2O + \underset{\text{Conine.}}{C_8H_{15}N}.$$

J. B.

On the Oxidation-products of Picoline. By JAMES DEWAR.*

THE picoline used in this investigation boiled between 130° and 140°; analyses of the platinum salts of portions boiling between those temperatures showed the fractions to be substantially picoline, with a possible trace of lutidine. As is well known, picoline is not acted upon by nitric or chromic acid, even at high temperatures; of other oxidizing agents, permanganic acid or its potassium salt seems to be the most powerful. The oxidation was performed in a large flask, which was connected with a reversed Liebig's condenser; for one operation the author took 150 grms. of potassic permanganate, 1½ litres of water, and 25 grms. of picoline. The mixture was heated to the boiling point, when a violent reaction set in, necessitating the removal of the source of external heat; the reduction of the permanganate was completed in half an hour.

The products of the reaction are ammonia, probably a small quantity of pyridine, carbonic, nitric, acetic, oxalic, and a complex of new acids, amongst which *dicarbo-pyridenic acid*, $C_5H_3N\left\{\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$, predominates; this body, after several recrystallisations from water, was obtained in colourless plates resembling naphthalene. It is a bibasic acid; the neutral ammonium salt is extremly soluble in water; the acid salt is less soluble and crystallises in fine silky needles. The mercury, copper, cadmium, and zinc salts are also readily soluble. The barium and calcium salts, which are also soluble, were obtained in minute prismatic needles, by adding the respective chlorides to a solution of the neutral sodium or ammonium salt. The silver salt of this acid is specially characteristic; it is obtained as a white gelatinous precipitate, which is insoluble in boiling water, and is not visibly affected by exposure to light.

* Chem. News, xxiii, 38.

On heating dicarbo-pyridenic acid it melts at about 210° C., frothing up and evolving a small quantity of carbonic anhydride, and emitting the characteristic smell of the bases of the pyridine series. When heated with soda lime the acid is decomposed and a basic substance is obtained, which is most probably pyridine.

Besides dicarbo-pyridenic acid, there are acids having a higher molecular weight formed by the oxidation of picoline, which have not been studied yet, as the quantities which the author had at his disposal were only small.

The author considers *pyridine*, C_5H_5N, the lowest member of this series of bases, as the nucleus from which all the other members are derived; just as all aromatic compounds are derivatives of benzol. Pyridine would thus be benzene in which nitrogen functions in place of the triad group $(CH)'''$.*

We thus have the following rational formulæ:—

Pyridine.	Methyl-pyridine, or picoline.	Dicarbo-pyridenic acid.
C_5H_5N	$C_5H_4N.CH_3$	$C_5H_3N \left\{ \begin{matrix} CO_2H \\ CO_2H. \end{matrix} \right.$

Dicarbo-pyridenic acid bears, therefore, the same relation to pyridine that phtalic acid does to benzene, and its formation from picoline is quite analogous to the formation of phthalic acid by the action of oxidising agents upon benzene, as shown by Carius.

C. S.

On Acridine. By Graebe and Caro.†

In purifying large quantities of anthracene, a small quantity of a basic substance (acridine) accompanies the crude hydrocarbon. To prepare it, crude anthracene, before it has been treated with solvents, is boiled with dilute sulphuric acid, and acid potassium chromate added to the filtered solution. An almost insoluble precipitate at once forms, soluble in a large quantity of boiling water. By several crystallisations, acridine is obtained in beautiful orange-yellow needles, or prisms, from which ammonia liberates the base. By washing with a little cold water and crystallising from hot water, the base, $C_{12}H_9N$, can be easily obtained pure. Pure acridine is colourless, crystallises in plates, volatilizes with aqueous vapour, melts and begins to sublime in plates at 107°, and distils unchanged at 360°. It is readily soluble in alcohol and in ether. It acts energetically even in very dilute solution on the sensitive parts of the skin, and on the mucous membrane. Its powder, inspired even in the smallest quantity, causes

* The same view has already been expressed by Koerner.—C. S.

† Ann. Ch. Pharm., clvii, 159.

sneezing. The salts of acridine are all yellow, or orange-yellow, although the pure base is colourless. They crystallise very readily, but, nevertheless, have not as yet yielded perfectly constant numbers on analysis. Very dilute solutions appearing colourless by transmitted light exhibit a magnificent blue colour by reflected light, which passes into green the more concentrated the solution is made, and disappears almost completely when the solution is of a deep yellow colour by transmitted light.

E. D.

Decomposition of Caffeidine by Barium Hydrate. By F. ROSENGARTEN and A. STRECKER.*

SOME years ago Strecker† showed that by the action of barium hydrate on caffeine, a new base was obtained, which he termed *caffeidine*. Its formation is explained by the equation—

$$C_8H_{10}N_4O_2 + H_2O = C_7H_{12}N_4O + CO_2.$$

At the same time methylamine and ammonia were given off, and the mother-liquors contained substances the nature of which was not determined. Otto Schultzen‡ has since communicated that the final products of the action of barium hydrate on caffeidine are—besides barium carbonate, methylamine and ammonia—barium formate, and a crystalline body of the composition $C_3H_7NO_2$. This latter formed crystalline salts with hydrochloric and sulphuric acids, but no double compounds with platinum chloride or gold chloride, and from this he concluded that it was neither sarcosine nor alanine, but the alanine corresponding to *paralactic* acid; against which view, however, is the fact noticed by himself, that when treated with nitrous acid, it does not yield *paralactic* acid, but a *nitroso*-compound, the calcium salt of which is represented by the formula $[C_3H_5(NO)NO_2]_2$ Ca + aq. Rosengarten and Strecker have re-examined this reaction, and find that in the main Schultzen is correct. They were able, however, to obtain both platinum and gold salts of the crystalline compound $C_3H_7NO_2$ (methylamidacetic acid), and find that these salts are identical both in composition and properties, with those prepared from ordinary sarcosine.

Both sarcosine prepared from creatine and that from caffeine were found to dissolve cupric oxide on boiling,—well formed blue rhombic crystals separating out as the liquid cooled; their composition is indicated by the formula $C_3H_6CuNO_2$ + aq. Finally the sarcosine from caffeine was converted into creatine by mixing its aqueous solution with

* Ann. Ch. Pharm., clvii, 1.

† *Ibid.*, cxxiii, 360.

‡ Zeitschr. f. Chem. [2], iii, 614.

a concentrated solution of cyanamide, with addition of a small quantity of ammonia. The creatine obtained was identical with ordinary creatine. Rosengarten and Strecker note that while Volhard (*Chem. Centralblatt*, 1869, 364) obtained only 20 pts. of creatine from 100 pts. sarcosine, they, by observing the conditions followed by one of them (Strecker, *Jahresb. für Chemie*, 1861, 530) in the preparation of glycocyamine, obtained a yield of 130 per cent. of recrystallised creatine. It is evident that the action of nitrous acid, as observed by Schultzen, is a further proof of the identity of the body $C_3H_7NO_2$ with sarcosine, when it is considered that those compounds which contain the NH_2 group are, by the action of nitrous acid, in general converted into *oxy*-compounds, whereas those in which methylamine, NCH_3H_2, is present yield *nitroso*-compounds:—

$$A.NH_2 + NO_2H = A.OH + OH_2 + N_2$$
$$A.NHCH_3 + NO_2H = A.N(CH_3)NO + H_2O.$$

The equation representing the decomposition of caffeine is the following:—

$$C_8H_{10}N_4O_2 + 6H_2O = 2CO_2 + 2NCH_5 + NH_3 + CH_2O_2 + C_3H_7NO_2.$$

Creatine similarly treated yields sarcosine, carbonic acid, and ammonia, but both methylamine and formic acid are wanting.

H. E. A.

On Acetopiperidine-Compounds. By K. Kraut.*

A mixture of 1 mol. chloracetic acid with 2 mols. aqueous piperidine was allowed to stand several days, the excess of piperidine distilled off, the residue shaken with silver oxide, and the filtrate freed from silver by hydrogen sulphide, then boiled so long as piperidine passed over, and finally evaporated to crystallisation. The product was then recrystallised from alcohol. The reaction may be represented as follows:—

$$2(C_5H_{10}HN) + Cl.CH_2.COOH + HOH = HO.C_5H_{10}HN.CH_2.COOH + C_5H_{10}.H_2N.Cl.$$

The compound $C_7NH_{15}O_3$, *acetopiperidine hydroxide*, forms colourless crystals belonging to the rhombic system, which by careful heating may be sublimed unchanged; it is readily soluble in water, less soluble in alcohol. By the action of cupric oxide on its aqueous solution, a copper salt is obtained, crystallising in blue plates, which contain 4 mols. H_2O. The dry salt has the composition $Cu(O.C_7NH_{12}O)_2$ and is therefore an acetopiperidine, and not a derivative of acetopiperidium hydroxide.

* Ann. Ch. Pharm., clvii, 66.

Acetopiperidium chloride, $Cl.C_5H_{10}.HN.CH_2.COOH$, is obtained by evaporating a solution of the hydroxide in hydrochloric acid. By mixing concentrated solutions of gold chloride and the above chloride, an aurochloride is precipitated of the probable composition—

$$3(HCl.AuCl_3).4C_7NH_{13}O_2.$$

A barium double salt, which may perhaps consist of $C_7NH_{13}O_2.BaCl_2$ was also prepared.

H. E. A.

On Strychnine-oxethyl Compounds. By R. MESSEL.*

R. MESSEL has prepared compounds of strychnine and quinine with ethylene hydroxychloride (C_2H_4OHCl). The strychnine derivative—$C_{21}H_{22}N_2O_2 + C_2H_4OHCl = C_{23}H_{27}N_2O_3Cl$—is readily soluble in water, from which it crystallises in white, glistening tufts, containing 1 mol. H^2O. Ammonia produces *no* precipitate in its solutions; potassium dichromate and concentrated sulphuric acid give a fine violet colour, which disappears after long standing. With platinum chloride it forms an orange-coloured crystalline double salt, $2C_{23}H_{27}N_2O_3Cl.PtCl_4$.—The sulphocyanate, iodide, nitrate, sulphate, and hydrate were all obtained by double decomposition from the chloride. A freshly prepared solution of the free base is without action on litmus paper, and entirely tasteless; its salts have at first a sweetish, and afterwards a sharp, bitter taste. With regard to the physiological action of the chloride, middle-sized frogs were killed by 3 to 4 mgrm. subcutaneously injected, and even much smaller doses caused total paralysis of the motor nerves, lasting for hours, and even days, while the muscles contracted powerfully on direct irritation.

H. E. A.

Decomposition of Morphine Acetate in Solution.
By JOHN M. MAISCH.†

ATTENTION is directed to the decomposition which a solution of this salt is apt to undergo on keeping for some time. A solution of 8 grains of the acetate in $\frac{1}{2}$ oz. of distilled water which had been set aside for several months had deposited a considerable quantity of brown matter, and from the liquid, which was of a pale brownish colour, a single crystal had separated, reaching from the surface of the liquid diagonally through the solution to the bottom of the vial. The crystal (which was alkaline, and contained neither acetic, carbonic, nor any mineral acid) proved to be pure morphine. The liquid was neutral to test-paper, but appeared still to contain a small quantity of acetate of morphine in solution.

W. H. D.

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* Ann. Ch. Pharm., clvii, 7.

† Pharm. Journ. Trans. [3], I, 664.

On the Preparation and Composition of Hyoscyamine. By H. HOEHN and E. REICHARDT.*

THE principal novelty in the method of preparation consists in precipitating the impure alcoholic solution of sulphate of hyoscyamine with tannin. The tannin compound being not insoluble in alcohol, a certain quantity is found in the liquid in which the precipitation is effected. The authors recommend the removal of the fatty oil from the henbane seeds (in which it exists to the extent of 26 per cent.) by means of ether. They give 0·0453 per cent. as the amount of hyoscyamine in henbane seeds.

To the description of appearance and behaviour towards re-agents already given by Geiger and Hesse, may be added the melting point, 90°, of hyoscyamine, its formation of precipitates with mercuric chloride, platinic chloride, and auric chloride; the gold precipitate appears to decompose after a time, with formation of hyoscinic acid.

The alkaloid gave on analysis, as mean numbers, 67·6 C., 9·0 H., 5·1 N., which lead to the formula $C_{15}H_{23}NO_3$. The *hydrochloride, platinochloride*, and *sulphate*, were analysed, with results expressed by the formulæ $C_{15}H_{23}NO_3.HCl + 2H_2O$, $2(C_{15}H_{23}NO_3.HCl).PtCl_4$, and $2(C_{15}H_{23}NO_3)_2H_2SO_4 + 2H_2O$, respectively.

By boiling for several hours with saturated solution of baryta, hyoscyamine breaks up into an acid and an amine, called by the authors hyoscinic acid and hyoscine.—Hyoscinic acid is described as crystallising in long glistening needles, which melt at 104°—105° and smell something like benzoic acid. The acid gave on analysis 65·1 per cent. C., 6·45 per cent. H., its barium salt 30·3 per cent. BaO, and 3·25 per cent. H_2O; results expressed by $Ba(C_9H_9O_3)_2 + 2H_2O$. Phloretic acid is an isomer of hyoscinic acid, but appears to be bibasic, and does not melt below 128° to 130° C. Hyoscinic acid appears rather to resemble atropic acid, $C_{18}H_8O_4$, obtained by Kraut in an analogous manner from atropine.

Hyoscine was obtained as an oily liquid, of strongly alkaline reaction, which crystallised by standing over sulphuric acid. As the whole quantity obtained did not exceed 0·3 grm., little was done beyond analysing the chloride and platino-chloride. $C_6H_{14}NCl$, and $2(C_6H_{13}N,HCl).PtCl_4$ express the composition of these substances, giving for hyoscine the formula $C_6H_{13}N$.

The breaking up of hyoscyamine may be represented thus:—

$$C_{15}H_{23}NO_3 = C_9H_{10}O_3 + C_6H_{13}N.$$

In an actual experiment 0·9 grm. hyosyamine gave, when boiled with

* Ann. Ch. Pharm., clvii, 98.

baryta, about 0·5 grm. acid, and 0·3 grm. of base. The above equation would require 0·56 grm. and 0·34 grm. respectively.

W. H. D.

On Chloracetamide and Iodacetamide. By N. MENSCHUTKIN and M. JERMOLAJEW.*

Monochloracetamide, $C_2H_2ClO.NH_2$. This body is prepared by cautiously mixing 1 volume of pure chloracetic ether† (boiling below 147°) with $2\frac{1}{2}$ volumes of concentrated ammonia, without shaking the mixture. After standing for 24 hours the ethereal layer becomes converted into a solid crystalline mass, which is purified by recrystallisation from the smallest possible quantity of water, the mother-liquor yielding a brown product nearly free from amide when evaporated. The product crystallises in thick prisms, easily soluble in alcohol and water, especially when boiling. It melts at 119·5° and solidifies at about 116°; sublimes very easily, even at the temperature of the water-bath, in broad, large needles; and distils in very small quantity, apparently undecomposed. Alkalis and baryta-water readily evolve ammonia on warming.

The *mercury-compound*, $(C_2H_2ClO.HN)_2Hg$, is formed by adding precipitated mercuric oxide to an aqueous solution of chloracetamide so long as the colour changes to white, then adding a large quantity of water, boiling, filtering, and exhausting the residue with boiling water. The air-dried compound does not lose weight over oil of vitriol, but begins to decompose at 100°. The compound is deposited from solution in fine needles or in warty masses made up of small needles. It dissolves with great difficulty in boiling water and is nearly insoluble in cold water. When it is heated to 170° a violent reaction occurs; chloracetamide sublimes, and mercury and carbon are left behind. The *silver-compound* cannot be obtained on account of its instability.

Iodacetamide is obtained by treating an alcoholic solution of chloracetamide with solid potassium iodide for a day at the ordinary temperature, with frequent agitation, and then evaporating the alcoholic solution. The amide crystallises from water, in which it is easily soluble, in fine colourless opaque prisms. When heated it melts, turns yellow, and decomposes, evolving fumes of iodine.

J. R.

* Zeitschrift für Chemie [2], vii, 5.

† Chloracetic ether is best prepared by distilling from a water-bath an alcoholic solution of chloracetic acid saturated with hydrochloric acid. The ether boils at 142°—147°, the last portions, however, distilling only above 150°.

On some Compounds of Aldehydes with Amides. By Dr. LUDWIG MEDICUS.*

Oenanthylidene-dibenzo-diamide $C_6H_{13}CH\left\{\begin{matrix}NHCOC_6H_5\\NHCOC_6H_5\end{matrix}\right.$ is formed, when two molecules of benzamide and one molecule of oenanthol are heated together for four or five hours; as soon as the benzamide is fused the reaction begins, and water is given off. The residue was dissolved in boiling alcohol, and, on cooling, the new compound separated in white crystalline flakes. It is insoluble in water, and sparingly soluble in ether. When carefully heated, it melts at 128°; it is perfectly neutral, and not acted upon by caustic potash, even on boiling. Cold hydrochloric acid does not affect it, but the *boiling* acid acts upon it, water being taken up, and benzamide and oenanthol being reproduced.

Oenanthylidene-dimonobromo-nitrobenzodiamide is formed by the action of nitrobenzamide upon oenanthol, and has the greatest resemblance to the preceding compound. It forms small white needles, not soluble in water, sparingly soluble in ether, readily in hot alcohol. It melts at 170° if carefully heated; decomposes when heated quickly; caustic potash has no action upon it; boiling hydrochloric acid decomposes it. By treating it with an alcoholic solution of ammonium sulphide, an amido-compound is formed, which was not obtained in the pure state.

Benzylidene-oxamide $C_2O_2\left\langle\begin{matrix}NH\\NH\end{matrix}\right\rangle C_7H_6$. Oil of bitter almonds does not act upon oxamide, but oxamethane does: the reaction takes place in two stages; first the oxamethane splits up into oxalic ether and oxamide, and the latter in the nascent state acts upon the aldehyde, thus:—

$$(1)\ 2C_2O_2\left\langle\begin{matrix}NH_3\\OC_2H_5\end{matrix}\right. = C_2O_2\begin{matrix}NH_2\\NH_2\end{matrix} + C_2O_2\left\langle\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right..$$

$$(2)\ C_2O_2\left\langle\begin{matrix}NH_3\\NH_2\end{matrix}\right. + C_7H_6O = C_2O_2\left\langle\begin{matrix}NH\\NH\end{matrix}\right\rangle C_7H_6 + H_2O.$$

The reaction takes place at 150°, and is finished after four or five hours. To obtain the compound in the pure state, the residue is first exhausted with ether to dissolve the greater part of the oil of bitter almonds which is still present, then treated with boiling alcohol, which leaves oxamide behind. The solution is evaporated, and the residue treated with a mixture of alcohol and ether, which removes oil of bitter almonds and oxamethane. The residue consists of benzylidene-oxamide, which is easily obtained pure by crystallisation from hot

* Ann. Ch. Pharm., clvii, 44.

water. It forms brittle and shining plates, containing ½ mol. water of crystallisation, which they lose at 100°. It is also readily soluble in alcohol, sparingly in ether, and crystallises from these solutions in silky needles. It is easily decomposed by boiling with caustic potash, oil of bitter almonds, potassium oxalate and ammonia being formed. Boiling hydrochloric acid attacks it but slowly. When heated it begins to decompose above 200°, and at a higher temperature it melts and undergoes complete decomposition.

C. S.

Poisonous principle of the Tutu Plant (Coriaria ruscifolia). By W. Skey.*

The poisonous principle of this plant does not appear to be of the nature of an alkaloïd. By treating the ground seeds repeatedly with alcohol a greenish-red coloured substance was obtained, which when acted upon by ether was separated into two parts, one, a green oil soluble therein; the other a resinous substance quite insoluble in that menstruum. The oil given to a cat, after a 12 hours' fast, in a dose of about 5 minims, produced vomiting and convulsions, from which, however, the animal gradually recovered.

As the symptoms agreed generally with those exhibited by cattle and sheep when poisoned by the Tutu plant, the author infers that this oil constitutes, or at least contains the poisonous principle of the plant. The oil appears to be a non-drying fixed oil, and to contain an acid peculiar to itself and quite distinct from the ordinary fatty acids; to this acid the author is inclined to ascribe the poisonous effects of the oil. Should this view prove to be correct, the matter would assume a peculiar interest, as affording another instance in which a non-nitrogenous oily body affects the system like a neurotic poison.

J. B.

On Curcumin, the Colouring Matter of Turmeric. By F. U. Daube.†

The substance hitherto described as the colouring matter of turmeric is a mixture of different resins with the pure compound, which the author has succeeded in obtaining in the crystalline state by the following simple process:—A strong current of steam was passed over coarsely powdered turmeric, to remove the essential oil, and the residue was washed with hot water as long as colouring matter was extracted, then dried, and treated with boiling benzol. On cooling, crude curcumin separated in crystalline crusts, which were pressed between filtered paper and dissolved in cold alcohol, a small quantity

* Pharm. Journ. Trans. [3], I, 568.

† N. Repert. Pharm. xx, 36, from Deutsh. Chem. Ges. Ber., iii, No. 11.

of a yellow body being left behind. To the filtrate a solution of neutral lead acetate was added, and then so much basic acetate that the solution just showed a faint acid reaction. The brick-red precipitate, after being washed, was suspended in water and decomposed by sulphuretted hydrogen. From the precipitate the curcumin was extracted with boiling alcohol, and the solution allowed to evaporate very slowly.

Pure curcumin crystallises in shining prisms, apparently belonging to the orthorhombic system, which by transmitted light appear of a hock or amber colour, and by reflected light are orange-red. The alcoholic solution is fluorescent, like tincture of turmeric; the spectrum of the reflected light does not show any alteration from the red end to F, but the blue, violet, and ultra-violet portions are replaced by a greyish green band, in which the lines H, L, M, N, &c., are distinctly visible. By analysing this modified spectrum with a prism it was found to contain very little red, and the blue end had nearly disappeared. This secondary spectrum agrees very nearly with that of uranium glass.

Curcumin begins to melt at 165°, and is completely decomposed at a higher temperature. It is very readily soluble in alcohol and ether, but these solvents cannot be used for extracting it from turmeric, as they also dissolve resinous matters. In benzol it is very little soluble (1 part in 2,000 parts), but as the resins are quite insoluble in this liquid, it has to be used to obtain the pure compound. It is also a little soluble in concentrated mineral acids, which however act on it. In alkalis it dissolves with a bright reddish-brown colour; acids precipitate from this solution the original substance; calcium- and barium-salts produce reddish-brown precipitates. The lead-compound, which has a bright red colour, is soluble in acetic acid, and is slowly decomposed by carbonic acid. The composition of curcumin is $C_{10}H_{10}O_3$. The analyses of the lead-compound did not give concordant results, but they make the formula $C_{20}H_{18}PbO_6$ probable.

Hot dilute nitric acid oxidizes curcumin to oxalic acid. Sodium amalgam decolorises the alcoholic solution completely. The colour reactions of pure curcumin are much purer than those of turmeric solution. The author employed curcumin-paper, prepared with Swedish filter-paper which was free from lime. Alkalis change the yellow into a brownish-red, which, after drying, assumes a violet tinge; dilute acids restore the original yellow. A solution of boric acid produces a pure orange, which appears only after drying; if the paper had been previously dipped in a dilute acid, the coloration became darker, as dilute acids alone produce a blackish tinge after drying. The orange colour is not changed by diluted acids, but dilute alkalies convert it into a blue, which soon changes into a dirty grey. By acting on curcumin with boric acid and concentrated sulphuric acid, E. Schlumberger

obtained a substance which he called *rosocyanin*, as its solution has the colour of a rosaniline salt, and its metallic compounds are blue. The author has repeated these experiments with pure curcumin, and has obtained the same results, but his investigation is not quite finished.

C. S.

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*Contributions to the Knowledge of Argemone Mexicana.**

THE first section of this paper contains an interesting historical account of the plant and its migration, by Flückiger, who also objects to some statements of Charbonnier on the purgative action of the oil obtained from the seeds of the Argemone. Flückiger did not find its action as a purgative so powerful as that of castor oil.

The oil was examined for volatile acids, by O. Frölich. $3\frac{1}{2}$ lbs. of oil were saponified with soda-ley, the solid soap was salted out, and the aqueous liquid treated with sulphuric acid, and distilled. The distillate was neutralised with soda, evaporated down, decomposed by sulphuric acid, and repeatedly shaken up with ether. The ethereal solution gave about 1 grm. of a liquid boiling above 100°. This went over between 140° and 240°. About $\frac{1}{2}$ grm. of a liquid boiling between 160°—190°, was obtained from it. It gave on analysis 55·8 per cent. C., and 9·4 per cent. H. A mixture of butyric and valeric acids would give numbers approaching these. The portion coming over above 190° became solid on cooling. It showed the melting point (120°), and several other properties of benzoic acid, but there was not enough for analysis. The aqueous liquid, exhausted with ether, appeared to contain acetic acid.

W. H. D.

Fluorescence of Peppermint Oil. By FLUCKIGER.†

FLUCKIGER states that 50 to 70 drops of peppermint oil shaken with one drop of nitric acid, sp. gr. 1·2, become faintly yellowish, brownish, and after an hour or two, exhibit a beautiful blue violet or greenish blue colour; by reflected light the liquid is of a copper colour and not transparent. The reaction may be hastened by the application of heat, or by adding a larger proportion of acid. All the samples of oil examined exhibited this behaviour, the colour varying, however, with different specimens; nevertheless, although this reaction is perfectly characteristic of peppermint oil, it appears not capable of being applied as a true test, since an admixture of 5 per cent. of oil of turpentine, for instance, did not prevent the appearance of the blue or green colour.

H. E. A.

* Arch. Pharm. [2] cxlv, 51.

† Pharm. J. Trans. [3], i, 682.

Analytical Chemistry.

Electro-thermic Methods of Analysis and Synthesis. By E. MULDER and F. C. E. von EMBDEN.*

FOR many experiments, such as the combustion of carbon or sulphur, the reduction of carbon dioxide by carbon, &c., a simpler arrangement than that previously described by the authors may be adopted.

If it is desired to burn carbon in oxygen, for instance, a large test-tube, or a flask, is partially filled with the gas over the mercurial trough, the volume being marked by means of a caoutchouc ring. Into this vessel is introduced a copper wire, carrying at its upper end a small dish made of clay, through the bottom of which it passes. To the extremity of the wire is attached one end of a fine platinum wire, which is wound round a fragment of charcoal, and connected by its other end to a copper wire passing through the dish, and dipping into the mercury in the vessel. The copper wire carrying the dish is insulated by a glass tube, bent into the form of an inverted siphon, with very unequal limbs, the longer limb reaching above the level of the mercury in the tube or flask, while the shorter projects above the surface of the mercury in the trough. This tube becomes partly filled with mercury in the act of introducing it, with its contained copper wire, into the vessel of gas. The apparatus being thus arranged, one pole of a battery (two Grove's elements are quite sufficient) is dipped into the mercury in the trough, and the other into that in the glass tube, whereupon the platinum wire becomes red-hot, and the charcoal is kindled.

Another method, applicable, however, to fewer experiments, consists in the use of a float, which may be made of clay. To burn sulphur in oxygen, for example, a copper wire passes through the float, being secured underneath, and carrying above a small dish of copper or clay, on which is a fragment of sulphur fused to a platinum wire, one end of which passes through a hole in the dish, and is fastened beneath, the other end being connected with an insulated copper wire passing through the dish and float, and secured to both. The vessel being partly filled with oxygen, and the height marked with a caoutchouc ring, the float is introduced, and rises to the surface of the mercury. One pole of the battery is connected with the mercury in the trough, the other with the insulated wire; the platinum wire then becomes red-hot, and the sulphur burns quietly.

J. R.

* Zeitschrift für Chemie [2], vii, 1.

A Method of Quantitative Analysis and Synthesis. By E. MULDER.*

THE principle of this method will be made clear by an example.

Analysis of gaseous Hydrogen Chloride by means of iron. A graduated glass tube closed at one end is partially filled with the gas over the mercurial trough, and the volume read off in the usual manner. Two copper wires, one of which is insulated by glass, are then introduced into the tube. One of these wires is coiled into a flat spiral at top; the other carries at its extremity a kind of brush, formed of a number of short pieces of iron wire of different lengths, secured to it by means of platinum wire. One pole of a battery of three Grove's elements being connected with the mercury in the trough, and the other with the insulated copper wire, the apparatus is adjusted with the hand, so that the ends of the iron wires are brought into contact with the copper coil, whereupon the iron begins to glow, and ferrous chloride is formed. When the volume of the gas ceases to contract, the wires are removed, and the volumes of the residual hydrogen is read off.

It is obvious that one of the wires may be of platinum, passing through the top of the tube, the other, which need not then be insulated, passing up through the mercury as before.

This principle, modified to suit particular cases, is applicable to the analysis of compound gases and vapours, such as hydrogen chloride, hydrogen sulphide, or water-vapour by means of iron, copper, &c.; or of mixtures of gases, such as oxygen and nitrogen by means of copper (method of analysing air). It is applicable further to the combination of gases, as hydrogen and oxygen, and of solid elements, as iron, carbon, sulphur, &c. It may also be employed to effect the combustion of carbon, iron, and other solids in nitrogen protoxide, nitrogen dioxide, &c.; or of gases by means of partially oxidized iron or copper wire, lead-chromate, and other solid compounds of oxygen; or of vapours, such as alcohol-vapour (method of organic analysis). Lastly, it is applicable to experiments on the dissociation of gases and vapours, such as ammonia or water-vapour by platinum, palladium, &c.

This method of experimenting is extremely well suited for lectures, the apparatus being simple, and the manipulation easy.

J. R.

On some Sources of Error in Volumetric Analysis. By R. R. TATLOCK.†

THE object of the author is to point out certain sources of error in volumetric analysis, and to indicate how they may be avoided. Reference is made to the contradictory statements of various experi-

* Zeitschrift für Chemie [2], vii, 2.

† Chem. News, xxiii, 13.

mentalists respecting the change of volume that takes place on mixing saline solutions with water. From the fact that the specific gravity of a mixture of a saline liquid and water is greater than its calculated mean, and from direct experiments, it is inferred that contraction does, as a rule, take place on admixture of a saline liquid with water. Strong solutions were found to contract proportionately far more than weak ones. Two sources of error are specially mentioned—the one arising from this contraction, and the other from the fact that vessels do not deliver in a given time corresponding volumes of water and saline solution, but rather less of the latter, the exact amount depending to some extent upon the sp. gr. of the solution. The first named source of error may be obviated, (1) by using as weak solutions as possible, and (2) by mixing the saline liquids thoroughly with the water before making quite up to the required bulk. The error caused by the adhesion of a saline liquid to the delivering vessel, may be obviated by graduating it in terms of the particular solution to be employed.

A. T.

On the Precipitation of Small Quantities of Phosphoric Acid by means of Ammonium Molybdate, together with a few Remarks on the Yellow Precipitate containing Silico-molybdic Acid. By E. RICHTERS.*

AMMONIUM molybdate deservedly enjoys the reputation of being an extremely delicate reagent for phosphoric acid. Its sensitiveness depends, however, upon well-defined conditions, which must be strictly complied with, if small quantities of phosphoric acid have to be determined. Among these is the absence of free hydrochloric acid, in anything like large quantities, whilst nitric and sulphuric acids do not interfere with the accurate precipitation of phosphoric acid within the usual limits of quantitative analysis.

It is otherwise, however, in the case of earthy minerals, &c., the solution of which usually contains extremely minute traces of phosphoric acid, together with much free acid and a large amount of salts (nitrates and sulphates). A large excess of ammonium molybdate has to be employed, in order to counteract the solvent power of distilled water on the free acid as well as on the salts. The sulphates and nitrates of the light metals, especially of the metals forming the strongest bases, are found to retard the separation of the precipitate, and require, therefore, the largest amount of ammonium molybdate. A 5 per cent. solution of the ammonium sulphate, acidulated with dilute nitric acid, on the other hand, acts rather favourably. Nitrates in general appear to assist the precipitation. Ammonium nitrate was especially observed to accelerate the formation of the yellow precipitate

* Dingl. polyt. J., cxcix, 183.

in a most extraordinary manner, and from very dilute solutions, the precipitation being accomplished also by a much smaller quantity of ammonium molybdate.

Standard solutions containing respectively—

(I) ·002 grm. and (II) ·010 grm. of phosphoric acid per litre; also solutions. (III and IV) containing the same amounts of phosphoric acid, dissolved, however, in ammonium nitrate (100 grms. per litre) were prepared. 10 c.c. of solutions I and II, to which 0·3 c.c. of a solution of ammonium molybdate had been added, remained perfectly clear on standing for several hours in a warm place. Solution III gave a precipitate on standing at the ordinary temperature for twelve hours; solution IV, after standing for 30 minutes only. The precipitation was complete after 20 hours, and the further addition of several cubic centimetres of ammonium molybdate to the clear filtrate produced no further precipitate, even on heating for 24 hours. On warming solution III, a precipitate was produced after the lapse of one hour, and on adding a further quantity of ammonium molybdate (about 2 c.c. for every 10 c.c. of solution), the sensitiveness of the reaction in the presence of the ammonium nitrate became practically unbounded.

The extent to which ammonium nitrate counteracts the solubility of the phospho-molybdate precipitate in solutions of the sulphates and nitrates of the alkalis and alkaline earths, as far as they are soluble (concentration 1 in 10, or, if less soluble, saturated solutions), was next ascertained, and it was found that ammonium nitrate assists the precipitation in a like ratio. Solutions containing much nitric acid required only about one-third the amount of the reagent in the presence of ammonium nitrate.

Richters proposes to conduct the determination of very small quantities of phosphoric acid in the presence of large quantities of nitrates and sulphates as follows:—The acid solution is diluted with water, so as to leave about 1 grm. of the salt in 10 c.c., or, if much ammonium sulphate be present, 1 grm. in 20 c.c. The solution is rendered slightly ammoniacal, and then once more acid (nitric acid). If a sufficient amount of ammonium nitrate be not already formed in this manner, an equal volume of a 20 per cent. solution of this salt is added, and the solution heated to 50° C., after the ammonium molybdate has been added. On adding ammonia to a thoroughly acid (nitric) solution, a certain amount of ammonium nitrate is formed (which may be readily estimated if the strength of the ammonia solution be known), and should be taken into account in diluting the solution to the above strength. The separation of the yellow precipitate is both rapid and complete, in fact, instantaneous, from solutions which contain only $\frac{1}{50,000}$ of the weight of the original salts.

Richters proposes to employ a slightly acidified 15 per cent. solution of ammonium nitrate, in the place of ammonium molybdate, for washing the yellow precipitate, or else a nitrate solution mixed with a few cubic centimetres of the ammonium molybdate. The precipitate obtained from the phosphate solutions containing much ammonium nitrate is distinguished by a somewhat brighter yellow colour.

Richters remarks, lastly, on the yellow precipitate produced by ammonium molybdate from solutions containing silicic acid, which is but slowly soluble in cold dilute ammonia, with separation of flakes of silicic hydrate, and not unfrequently accompanies the magnesian precipitate, to which it gives its flaky appearance.

W. V.

Estimation of Sulphur in Cast Iron. By W. H. Elliott.*

This method depends on the evolution of the sulphur as sulphuretted hydrogen, the absorption of the latter in solution of pure soda (prepared from sodium), and the determination of the sulphuretted hydrogen in the acidified soda-solution by means of standard solution of iodine.

W. V.

Estimation of Phosphorus in crude Pig-Iron, Steel, and Malleable Iron. By F. Kessler.†

The method is based upon the precipitation of the iron in the state of ferrous chloride by potassium ferrocyanide, $FeCl_2 + K_4FeCy_6 = Fe''K_2FeCy_6 + 2KCl$, and the separation of the phosphoric acid from the filtrate in the form of ammonio-magnesic phosphate. As the process involves filtration from a bulky precipitate—an operation known to every chemist as being among the most tedious—the author proposes to collect only the first half of the filtrate for precipitation with magnesia mixture. Assuming an iron to contain 1 per cent. of phosphorus, in order to obtain a precipitate of magnesium pyrophosphate amounting to ·100 grm., 2·793 grms. of crude iron would have to be operated upon; or, as only half the bulk of the filtrate is to be employed, the quantity of the metal would have to be doubled. This quantity of metal (5·6 grms.) after solution in acid, requires no less than 42 grms. of crystallised potassium ferrocyanide. The ensuing precipitate weighing at least 34 grms., exclusively of chemically combined water, it became necessary to make a correction for bulk. 11 grms. of soft iron wire were dissolved in hydrochloric acid, and the solution diluted to 500 c.c. 84 grms. of crystallised potassic ferrocyanide were dissolved in water, and the solution likewise made up to 500 c.c. The specific

* Chemical News, xxiii, 61.

† Chemical News, xxiii, 76.

gravity of the iron solution was found to be 1·055, that of the ferrocyanide solution 1·093. 250 c.c. of each solution were mixed, and the bulk of the mixed solutions was then found to be equal to 505 c.c. The filtered liquid had a specific gravity of 1·033: hence the bulk of the liquid was calculated as follows:—

$$250\ (1{\cdot}055 + 1{\cdot}093) - 34 = 503 \text{ grms.},$$

$$\text{and } 505 - \frac{503}{1{\cdot}033} = 18 \text{ c.c.}$$

In order, therefore, to work only with 250 c.c.—one-half the filtrate—the liquid containing the precipitate has to be first made up to 518 c.c. This quantity may be varied, according to the purity of the metal, from 517·5 to 518·5 c.c.

Previous to dissolving the iron in acid, it should be suitably comminuted; crude pig-iron, for instance, should be broken up in a steel mortar and passed through a sieve, the meshes of which are 0·5 mm. apart. 5·6 grms. of the metal are then treated in a covered porcelain vessel with 60 c.c. of nitric acid, sp. gr. 1·2; the solution is evaporated to dryness; and the residue strongly ignited (best in a muffle) to bright redness, first in the porcelain vessel, next in a platinum crucible, in order to oxidize the carbon. It is then dissolved in 35 c.c. of hydrochloric acid, sp. gr. 1·19, with the aid of a gentle heat. A residue of silica is left. The acid solution so obtained is washed into a flask, without being previously filtered, and diluted to about 200 c.c. A current of sulphuretted hydrogen is next passed, in order to reduce the ferric to ferrous salt, a method of reduction which Kessler prefers to the reduction by means of an alkaline sulphite.

200 c.c. of a solution of potassium ferrocyanide (strength 210 grms. of the crystallised salt per litre) are next added, and the bulk of the liquid made up to exactly 518 c.c. The precipitate is filtered off. From 20–30 c.c. of the first portion of the filtrate usually pass through turbid, and may be rejected. 250 c.c. of the clear filtrate are collected in a graduated flask, and precipitated in the usual way, by adding, in a beaker, 10 c.c. of magnesia mixture (strength 200 grms. of magnesium sulphate per litre). Kessler observes that the precipitate is always covered with a greyish flocculent substance, which he removes by throwing the precipitate and the body just referred to on a small filter and washing with ammonia of sp. gr. 0·98. He next dissolves the precipitate which adheres to the sides of the beaker, and also the portion contained on the filter, in nitric acid of sp. gr. 1·035, when a bluish coloured insoluble cyanogen-compound is left behind. The phosphate is reprecipitated by means of ammonia, collected on a small filter, and washed with ammonia of sp. gr. ·98, until on testing no more chlorine is detected. It is then dried, ignited, and weighed as magne-

sium pyrophosphate, ·100 grms. of which salt correspond to 1 per cent. (or, more correctly, to ·9975 per cent.) of phosphorus. The author states that he found the method correct in every respect, and suitable for all practical purposes, and that he prefers it to the molybdic acid method for the estimation of phosphorus in crude pig-iron, steel, and malleable iron.

W. V.

Estimation of Zinc in Galvanized Iron. By THOMAS T. P. BRUCE WARREN.*

THE zinc in galvanized iron exists in two states; firstly, part of the zinc forms an alloy with the iron; and secondly, to this alloy a greater or lesser quantity of zinc adheres mechanically. Only the part of zinc forming the alloy is necessary for the protection of the iron. This combined zinc cannot be removed from the iron by mercury, but is nevertheless capable of uniting with a definite proportion of that metal, 7 parts of this combined zinc taking up 11 parts of mercury. On heating the iron, the mercury is again volatilised. On the other hand, all the uncombined zinc can be removed by means of mercury. Let then a piece of galvanized iron be taken, weighed, cleaned with dilute sulphuric acid, and immersed for from 4 to 8 hours in mercury; it will be found that part of the zinc has been removed, part has remained on the wire together with the mercury absorbed. The piece is next taken out of the mercury, well rubbed with chamois leather, and again weighed, after which it is heated in a non-oxidizing flame, and the weight once more taken. The difference between the first and third weighings will be the uncombined zinc, while the difference between the second and third weighings, when multiplied by 7 and divided by 11, gives the combined zinc. This process, moreover, reveals all imperfections in the zinc coating, since no mercury adheres firmly to such places.

A. D.

On a Mode of distinguishing the Deposit from Reinch's Process from Salts of Mercury. By JAMES ST. CLAIR GRAY.†

THE coated slip of copper is rubbed with a flat piece of pure gold. If the deposit on the copper contains mercury, the gold becomes marked with a clear white shining crust, which is removable by nitric acid.

C. H. G.

* Phil. Mag. [4], xli, 132.
† Chem. News, xxxiii, 73.

Estimation of Urea by means of Sodium Hypobromite. By G. HÜFNER.*

HYPOCHLORITES, as is well known, decompose ammonia compounds, with evolution of nitrogen, and Wöhler† based upon this reaction a method for determining the amount of ammonia in guano. It consists in measuring the nitrogen which a weighed quantity of guano yields when treated with a solution of bleaching powder, the amount of ammonia being calculated from the volume of nitrogen which is given off.

Urea is acted upon in a similar manner: it is converted by the hypochlorous acid into free nitrogen, water, and carbonic anhydride, 1 grm. of urea corresponding to 370 c.c. of nitrogen (at 0° C. and 760 m.m. pressure).

E. W. Davy‡ described in 1854 a method—afterwards somewhat modified by Leconte—by which he effected (although imperfectly) the decomposition of the urea and the collection and measurement of the nitrogen in a graduated cylinder over a saturated solution of common salt.

W. Knop proposed to employ, instead of sodium hypochlorite, a solution of barium or sodium hypobromite, an oxidizing agent which is at once more effective and more stable, and a solution of which is readily prepared when required.

The preparation of sodium or barium hypobromite is described by Knop§ as follows: 600 grms. of barium hydrate are placed in two litres of water and are shaken up with 100 c.c. of bromine. On adding a solution of 300 grms. of barium hydrate in one litre of water (prepared by dissolving the hydrate in warm water), the bromine disappears and a golden-yellow solution is obtained, which probably contains barium bromate and bromide, as well as bromite and hypobromite. Sodium hypobromite is obtained by dissolving 100 grms. of sodium hydrate in 250 c.c. of water and leaving the solution to cool, before adding 25 c.c. of bromine. 50 c.c. of this solution, diluted with 200 c.c. of water, suffice to liberate 130 to 150 c.c. of nitrogen from a solution of sal-ammoniac.

The instrument devised by Knop—known under the name of *azometer*—renders it possible to determine urea rapidly and readily, and to complete within 15 to 20 minutes several determinations with sufficient accuracy.

Hüfner now proposes to modify Knop's method, so as to employ

* J. pr. Chem. [2], iii, 1.

† Prakt. Uebungen in der Chem. Analyse, Goettingen, 1853.

‡ Phil. Mag. [4], vii, 385.

§ Fresenius Zeitschr. f. Analyt. Chem ix, 2, p. 225.

a gentle heat in order to complete the re-action, securing at the same time the advantage of not having to mix the urea solution and the oxidizing agent, before the gas can be collected. On heating the hypobromite solution, oxygen is however evolved as well, and the mixed gases (nitrogen and oxygen) are therefore collected in a graduated cylinder. A urea solution is placed in the lower part of a mixing apparatus, shut off from the part containing the concentrated hypobromite solution by means of a wide-bore glass stop-cock. A glass cup, from 4 to 5 c.m. in depth, is fitted to its neck by means of a caoutchouc ring, over the open end of the mixing vessel, which reaches somewhat above it, and delivers the evolved gases into the mouth of the inverted measuring cylinder, which is about 30 c.m. long, and 2 c.m. wide.

The lower part of the mixing apparatus, below the glass stop-cock, has a diameter of 1·5 c.m., and holds about 10–11 c.c. of urea solution. The bore of the glass stop-cock should not be less than 7–8 mm. The upper portion of the mixing vessel is large enough to hold about 100 c.c. of sodium hypobromite, diluted with its own bulk of distilled water. The glass cup is filled with a saturated solution of common salt, over which the measuring cylinder, filled with distilled water, is inverted and fitted into its position. On opening the glass stop-cock, the specifically heavier hypobromite solution mixes rapidly with the urea solution, and a brisk evolution of gas ensues. The decomposition is assisted towards the end by plunging the lower part of the mixing vessel into hot water. A small quantity of oxygen has to be determined in the usual way by transferring the gases over mercury and absorption with pyrogallic acid.

The published experiments approximate closely to the theoretical percentage of nitrogen in urea.

The author adds, in conclusion, some speculations on the composition and constitutional formulæ of other nitrogenous bodies, such as hippuric acid, ethylamine, aniline, conëine, nicotine, asparagine, uric acid, creatine, and others, for which we must refer to the original paper.

W. V.

Detection of Alcohol in Chloroform and Chloral Hydrate. By HAGER.

HAGER has carefully examined* the method for the detection of ethylic alcohol described by (A. Lieben *Ann. Ch. Pharm. Supp.* viii, 2), based on the formation of iodoform, and finds it extremely delicate and capable of detecting $\frac{1}{2000}$ of alcohol in a liquid after about one day's standing. He uses the following reagents: 1. A solution of potassium iodide in 5 to 6 times its weight of water, supersaturated with iodine;

* Pharm. J. Trans. [3], i, 683.

2. A ten per cent. solution of potassium hydrate. To detect alcohol in *chloroform*, 2 vols. of the latter are shaken up with 5 to 10 vols. of water of about 50° C.; the liquid is then poured on a filter previously saturated with water; to the filtrate are added 5 or 6 drops of the potash solution, and the whole is heated to about 50° C.; the iodide solution is then added drop by drop, with gentle agitation, until the colour of the liquid remains brown, and finally, it is carefully decolorised by the addition of potassium hydrate and set aside to deposit. After 12 to 24 hours, the sediment is examined under the microscope, and the iodoform crystals recognised by their star-shaped form.

The presence of alcohol, or rather of chloral alcoholate in *chloral hydrate* may be detected in a similar manner.

Schering (*ibid.*) calls attention to other distinctions between chloral hydrate and alcoholate:—the former when warmed with twice its vol. of water dissolves, but the latter melts without solution, and solidifies again on cooling. Sulphuric acid remains colourless when warmed with the hydrate, whereas it turns brown with the alcoholate. No reaction or only a very slight one ensues on warming the hydrate with nitric acid, sp. gr. 1·2; the alcoholate is violently attacked, and nitrous fumes are evolved in abundance.

H. E. A.

Examination of Flour. By W. Danckwortt.*

The author has endeavoured to ascertain approximately the amount of wheat-flour present in what was declared and taxed as rye-flour. The amount of residue (gluten) left after washing out the starch and soluble matter from different mixtures of wheat and rye-flour, was determined; mixing the flour with well washed wheat-bran appears to facilitate the drying of the residue. The bag in which the sample is put, the flour and bran employed, are all thoroughly dried in the water-oven; as is also the gluten left by the washing. 10 grms. rye-flour mixed with 1 grm. wheat-bran, placed in a bag of silk bolting-cloth of a certain fineness, and washed with distilled water, until the water was no longer milky, gave, after subtracting the weight of the bag and bran, a residue of 0·5—0·8 per cent.; pure wheat-flour, similarly treated, gave 7·0—8·0 per cent. residue; mixtures of 3 p. rye-, with 1 p. wheat-flour, 1·0 to 2·0 per cent.; mixtures of equal weights of rye and wheat-flour gave 3·0 to 3·5 per cent. residue. These numbers were the mean of several experiments. The suspected flour similarly treated gave, in seven experiments, a residue varying from 1·0—2·2 per cent. This would be given by a mixture of 70—75 per cent. rye-flour, with 25—30 per cent. wheat-flour.

* Arch. Pharm. [2], xx, 47.

Microscopical examination of mixtures of the two flours, gave very doubtful results. W. H. D.

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*Analysis of Milk.** By J. A. WANKLYN.

THE "British Medical Journal" reports the following result of an analysis of the contents of a tin of Newnham's condensed milk.

Water	19·0
Casein	10·0
Ash	2·0
Fat	69·0
Milk-sugar	
Cane-sugar	

There appeared to be about as much fat as casein. From this analysis it follows that one pound of the condensed milk contains the solid constituents of from three to four pounds of fresh milk.

In the course of an examination of milk undertaken for the "Milk Journal," the observation was made that there is a source of inaccuracy in the ordinary methods of examining milk hitherto quite unsuspected. It was found that the exact molecular condition of the casein influenced the specific gravity of the milk, in other words, that samples of milk of the same strength varied in specific gravity according to the molecular condition of the casein. The following examples are given to show how this may cause a want of correspondence between the specific gravity of milk, and the amount of its solid contents. The specimens of milk had been kept in corked bottles for four days.

	Sp. gr. at 60° F.	Per cent. of solids dried at 212° F.	Per cent. of ash.
Sample A	1·0004	11·34	0·94
,, B	0·9960	10·48	0·75
,, C	1·0184	8·92	0·66

To be of any value at all, the specific gravity must be taken while the milk is very fresh, for when milk is kept for two or three days, even in a closed vessel, the density falls in a very remarkable manner. It is therefore proposed, in judging of the strength of milk, to adhere to the method of evaporating to dryness in the water-bath, and weighing the residue. J. B.

* Pharm. Journ. Trans. [3], I, 605.

Technical Chemistry.

*Preparation of Hydrogen Gas.**

THE Journal of the Society of Arts states that M.M. Tessié du Motay and Maréchal have lately discovered a new and economical method of producing hydrogen gas. The process consists in heating the hydrates of the alkalies and alkaline earths with coke, coal, charcoal, &c., to a red heat, whereupon carbonic acid and hydrogen are given off abundantly; and as the decomposed hydrates, especially that of lime, can be used indefinitely, by simply remoistening them with water, the method is very economical. In this operation the hydrogen gas is generated without any special production of steam, and may thus be produced without any other generating apparatus than the retorts themselves; and as these retorts are not exposed to the direct action of the steam, they are not subject to any interior deterioration. This process, it is said, in conjunction with the method of obtaining cheap oxygen from the manganates of soda, discovered by the same chemists, is likely to create a revolution in many industries, and especially in metallurgy.

J. B.

On the Application of certain Fluorine-compounds for the Preparation of Frosted Glass for Photographic Purposes. By E. SIEGWART.†

IN place of aqueous hydrofluoric acid for etching glass, the author recommends a solution of eight parts of an alkaline fluoride dissolved in 100 of water, and mixed just before using with one part oil of vitriol. Before immersion in this bath, the glass requires to be cleaned in another made with potassium dichromate and sulphuric acid, to remove all traces of organic matter from its surface. A few hours at ordinary temperatures suffice to produce a fine glistening frost.

The rest of the paper contains details concerning the preparation and use of etching-wax, for producing patterns and figures.

C. H. G.

On the Constitution of Ultramarine. By W. STEIN.‡

DOES ultramarine, as a whole, constitute a chemical compound, and in what state of combination does the sulphur exist therein?

Examining the latter point, the author rejects the idea of the sulphur

* Pharm. Trans. [3], I, 566.
† Dingl. Polyt. J., cxix, 222.
‡ Journ. pr. Chem. [2], iii, 39.

existing either as hyposulphite, sulphide, or polysulphide of sodium, and while admitting the presence of sodic sulphite in most samples of ultramarine, considers its presence accidental, the essential sulphur constituent being aluminium sulphide.

He finds that aluminium sulphide exists in two forms, as a crystalline colourless (yellow) mass, and as an amorphous black powder. The black modification arises when the body is formed at comparatively low temperatures, or when the presence of foreign matter between the particles prevents them fusing together.

He considers that this last condition obtains in the ultramarine manufacture, and that the characteristic blue colour of the body is due, not to its chemical composition, but to its mechanical structure—that it owes its colour indeed to the same causes which give a blue tint to a mixture of lamp-black and milk, &c.

He, therefore, concludes that ultramarine (blue) consists of a white (ground) mass, with which black aluminium sulphide is mingled in a state of molecular division.

White ultramarine he regards as the blue compound, the colour of which is compensated by the orange-red of sodium sulphide present with it, and the green pigment as arising from the conversion (partial?) of the orange-red sodium sulphide into sodium bisulphide, whereby yellow and blue occurring together give rise to green. C. H. G.

The Effects of Cold upon the Strength of Iron. By W. Brockbank.*

The bars of pig-iron employed were made from a mixture of four pig-irons of the highest class, added to some good scrap-iron, so as to insure a sounder and more regular casting; all the bars were cast from one ladle. The testing machine used was a powerful lever or steel-yard, the bars having a three-foot bearing. The results showed a gradual and considerable decrease of strength in the bars with the increase of cold below the freezing point. They also lost their elasticity in a similar degree.

	Tension.		Tension.	
	At 20°.	At 80°.	At 20°.	At 80°.
	2142 lbs.	2142 lbs.	16½ twists.	14½ twists.
	2114 ,,	2058 ,,	15½ ,,	14½ ,,
	2114 ,,	2086 ,,	9 ,,	13½ ,,
	2142 ,,	2086 ,,	14½ ,,	14½ ,,
	2114 ,,	2128 ,,	16 ,,	12½ ,,
	2114 ,,	2086 ,,	18½ ,,	14½ ,,
Total ..	12640 ,,	12586 ,,	90 ,,	83½ ,,
Average	2123·3	2097·6	15 ,,	13·9 ,,

* Chem. News, xxiii, 62.

Mr. Brockbank refers to the general experience of ironfounders, and cites instances of breakages of castings during frosty weather, showing that the strength of cast iron is very materially lessened by severe cold. Experiments were also made to test the effect of frost upon the tensile strength of wrought iron. The methods used by Kirkaldy, viz., torsion and gradual tensile strain, did not give a true result, as the iron tested worse when warm than when frozen. The simple test of the striker's hammer was then resorted to, and a number of experiments was described, showing "short" crystalline fracture in the iron without any appearance of fibre, whilst the same iron,—a strip of boiler plate,—after being slightly warmed to "dispel the frost," was exceedingly tough and fibrous, showing a good fibrous fracture.

Rails in course of manufacture for East Indian railways, at the Darlington Iron Company's Works, failed to pass the required test in frosty weather, whereas at ordinary temperatures a failure was a very rare occurrence. Rails were heated to 120° F., others were tested at the temperature of 26° F. The following table shows the results :—

Test of East Indian Railway Rails, 82 *lbs. per yard, November* 29, 1869, *tested by a Falling Weight of* 2,000 *lbs.; Centres of Support* 3 *feet* 6 *inches apart.*

No.	Number of blows.	Height of falls. ft.	Height of falls. in.	Permanent set.	Temperature.	Remarks.
1	First blow....	5	0	7–16ths ..	120°	Not broken.
	Second „	5	0	3-4ths		
	Third „	7	0	.. ..		
2	First „	5	0	3–8ths	Do.	Ditto.
	Second „	5	0	13–16ths ..		
	Third „	7	0	.. ..		
3	First „	5	0	3–8ths	Do.	Ditto.
	Second „	5	0	13–16ths ..		
	Third „	7	0	.. ..		
4	First „	5	0	3–8ths	Do.	Ditto.
	Second „	5	0	7–8ths		
	Third „	7	0	.. ..		
5	First „	5	0	3–8ths	26°	Broke with 2nd blow.
	Second „	5	0	Broke		
6	First „	5	0	3–8ths	Do.	Passed test.
	Second „	5	0	5–8ths		
7	First „	5	0	3–8ths	Do.	Broke with 2nd blow.
	Second „	5	0	Broke		
8	First „	5	0	3–8ths	Do.	Ditto.
	Second „	5	0	Broke		
9	First „	5	0	Broke	Do.	Broke with 1st blow.
10	First „	5	0	3–8ths	Do.	Broke with 2nd blow.
	Second „	5	0	Broke		

All the experiments adduced prove that iron becomes much weaker, both in its cast and wrought state, under the influence of low temperatures. It loses its toughness, becomes quite brittle under sudden impact, and changes its structure from fibrous to crystalline. W. V.

On the Production of Alloys of Iron and Manganese, and on their Application to the Manufacture of Steel. By F. Kohn.*

The author, after referring to Heath's patent in 1839, for the employment of manganese in the manufacture of steel, and to the use, of late years, of the Spiegeleisen of Rhenish Prussia, and other ferro-manganese alloys in the Bessemer, Siemens-Martin, and other processes, proceeds to describe the process of Henderson of Glasgow. This process, which has been at work for some time at the Phœnix Foundry, Glasgow, consists in reducing upon the open hearth of a Siemens' furnace a mixture of carbonate of manganese and oxide of iron in presence of excess of carbon, by means of a neutral or reducing flame.

The furnace bottom is of ground coke, consolidated and baked up to form a crucible on a large scale. The charge of finely ground oxides mixed with powdered charcoal or coke, is heated to redness for several hours. It thus becomes converted into a metallic sponge which contains the reduced metals from both oxides, and is then run down to a regulus by raising the temperature to a full white heat. The quantity of manganese in the alloy depends chiefly upon the high temperature obtained at this latter stage of the process: hence the necessity of employing a Siemens' furnace, by which a high reducing temperature can readily be obtained.

Though considerable loss occurs, owing to the action of the silica in the ores used, upon the manganese, yet with proper selection of materials, an average of 20 per cent. to 30 per cent. of manganese is obtained in the alloy.

An ordinary-sized furnace, worked by one man, can produce 15 cwt. of ferro-manganese every 24 hours.

The cost by this process the author states to be about £7 per ton for alloy containing 20 to 25 per cent. of manganese; this is exclusive of royalties, the amount of which per ton the author does not state. The author concludes by pointing out, that not only will the manufacture of these ferro-manganese alloys prove a profitable accessory to every Bessemer steel works in the country, but that it will also make these works independent of the fluctuations and uncertainties of the foreign supply. C. G.

* Journal of the Iron and Steel Institute, Feb., 1871, 70.

Observations on the Manufacture of Vermilion. By M. ALSBERG.*

IN manufacturing vermilion by Martin's process, two stages are to be observed, first, the formation of the amorphous black sulphide, and, second, the conversion of this into the crystalline red modification by the successive solution of the black sulphide by the alkaline sulphide present, and its deposition in the red form. The crystals of red sulphide so obtained are rhombohedrons, approaching a cube. They are doubtless the primitive rhombohedrons observed on the native crystals, R on R 92° 36′. The solubility of sulphide of mercury in alkaline sulphides constitutes a source of loss of from 5 to 8 per cent. of the mercury employed in this process. C. H. G.

Black Lustre Colour for Sugar-paper. By Dr. KIELMEYER.†

8 lbs. ordinary glue, 16 lbs. water, 1 lb. potato starch, $5\frac{1}{2}$ lbs. water, $5\frac{1}{4}$ lbs. Campechy extract of 6° Baume, 1 lb. 2 oz. green vitriol, $8\frac{3}{4}$ lbs. brown glycerin; all boiled together, and stirred when cold. Paper *once* painted with this mixture acquires, when dry, a fine bright black surface, remains supple, and does not exhibit a tendency to get sticky. If it be desired to render the paint thicker or thinner, the starch and the glue must be increased or diminished in the same proportion, or the lustre will be spoiled. C. H. G.

"*Sucrate of Hydrocarbonate of Lime*" *applied to the purification of Sugar-cane Juice.* By BOWIN and LOISEAU (Chem. News, xxiii, 19).

Preparation of quickly-hardening coloured Cements. By R BOETTGER.‡

WHEN finely-pulverized chalk is stirred into a solution of soda-water glass of 33° B., until the mixture becomes thick and plastic, a cement is obtained which will harden in between six and eight hours, possessing an extraordinary durability, and alike applicable for domestic and industrial purposes.

If any of the following substances be employed besides chalk, differently-coloured cements of the same general character are obtained.

1. Finely pulverized, or, better still, levigated stibnite (grey antimony or black sulphide of antimony), will produce a dark cement, which, after burnishing with an agate, will present a metallic appearance.

* Chem. News, xxxiii, 73.
† Dingl. Polyt. J., cxcix, 233.
‡ Pharm. J. Trans. [2], iii, 19.

2. Pulverized cast-iron, a grey cement.

3. Zinc-dust (so-called zinc-grey), an exceedingly hard grey cement, which, after burnishing, will exhibit the white and brilliant appearance of metallic zinc. This cement may be employed with advantage in mending ornaments and vessels of zinc, sticking alike well to metals, stone, and wood.

4. Carbonate of copper, a light green cement.

5. Sesquioxide of chromium, a dark green cement.

6. Thénard's blue (cobalt blue), a blue cement.

7. Minium, an orange-coloured cement.

8. Vermilion, a splendid red cement.

9. Carmine-red, a violet cement.

On a curious property of Gun-cotton. By L. BLECKRODE.*

A FLAME may be applied to gun-cotton which has been previously wetted with carbon bisulphide, without explosion taking place. Only the latter substance takes fire immediately, the gun-cotton remaining apparently intact amidst the burning bisulphide, presenting almost the aspect of a mass of snow slowly melting away. Ether, alcohol, and benzol may be employed with the same result. The author considers this slow combustion, which takes place when the cotton is moistened with carbon bisulphide or any other volatile liquid, to be a most direct and satisfactory proof in favour of the conclusion to which Professor Abel was led by his researches, viz., that if the gases resulting from the first action of heat on gun-cotton upon its ignition in open air, are impeded from completely enveloping the burning extremity of the gun-cotton twist, their ignition is prevented; and as it is the comparatively high temperature produced by their combustion which effects the rapid combustion of the gun-cotton, the momentary extinction of the gases, and the continuous extraction of heat by them as they escape from the point of combustion, renders it impossible for the cotton to continue to burn otherwise than in a slow and imperfect manner, undergoing a transformation similar in character to destructive distillation. A piece of phosphorus placed in the moistened mass of gun-cotton, is melted and even boils during the combustion, but does not burn, as it is prevented from contact with the oxygen till all the gun-cotton has disappeared. He suggests that gun-cotton should be preserved under carbon disulphide or benzol, by which the danger in case of fire is eliminated. Should the liquid become ignited, the cotton will be only slowly destroyed. H. E. A.

* Phil. Mag. [4], xvi, 39.

On the recovery of Tartaric and Oxalic Acids from the Residues of the "Discharge" Process, and on Eau de Labarraque as a substitute for Chloride of Lime in discharging Turkey Red. By ARMAND MÜLLER.*

WHEN cloth which is in parts impregnated with one or both of the above-named acids, is passed through the discharge vat, which contains chloride of lime, with a greater or lesser excess of lime, a well-known decomposition takes place, and the acids are converted into their calcium salts, which, being insoluble, settle together with the excess of undissolved lime at the bottom of the vat. If the slimy deposit so produced be allowed to remain in the working vat for some weeks, with frequent agitation, it becomes continually richer in the salts, and poorer in free lime, till it attains even such a percentage of the former as 65·5 per cent. calcium tartrate, and 18 per cent. calcium oxalate.

From this mixture, washed and somewhat diluted with water, the acids are liberated by addition of a previously determined quantity of sulphuric acid of 1·568 sp. gr., and after stirring and boiling with as much more water as is equal to the weight of the original deposit, the liquid is separated from the calcium sulphate by help of a centrifugal machine. Any excess of sulphuric acid contained in the liquid is removed by boiling with barium tartrate.

This method is still better when chloride of soda (eau de Labarraque) is employed in the discharging vat in place of the chloride of lime. As the tartrate of soda remains in solution, it is only necessary to add from time to time, a sufficient quantity of chloride of lime solution, to precipitate all the tartaric acid as a lime salt, and to restore the original working strength of the vat. In this case the precipitate will contain no calcium hydrate or carbonate, and consequently a great saving of sulphuric acid will be effected.

A further advantage is found to follow the use of the soda solution, namely, that the whites are whiter, and the reds are less injured, than when the chloride of lime is employed.

C. H. G.

* Chem. Centr. 1871, 134.

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Elected March 30, 1871.

PRESIDENT.

E. FRANKLAND, D.C.L., F.R.S.

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PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XIV.—*Communications from the Laboratory of the London Institution. No. I.—On the Formation of Sulpho-acids.*

By Henry E. Armstrong.

(Preliminary Notice.)

Occupied with an investigation into the constitution of sulphuric acid, the views on which are, as is well known, even at the present moment, extremely conflicting, my attention was soon drawn to the body discovered by Prof. Williamson, viz., *chlorhydric sulphate* (sulphuric chlorhydrate, sulphuric oxychloride) SO_2HOCl, and particularly by a somewhat remarkable reaction noticed by Karl Knapp,* who found that the chief product of its action on benzene was *sulphobenzide*,—*sulphobenzolic chloride* and *sulphobenzolic acid* being likewise formed, but in relatively very small quantity:—

$$2C_6H_6 + SO_2.HO.Cl = \left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}SO_2 + OH_2 + HCl.$$

$$C_6H_6 + SO_2.HO.Cl = SO_2.C_6H_5.Cl + OH_2.$$

$$C_6H_6 + SO_2.HO.Cl = SO_2.C_6H_5.HO + HCl.$$

It was presumable that sulphobenzolic acid would be the main product; the reverse was actually the case. This led me to commence a series of experiments to determine, if possible, the conditions under which the one or the other of the above reactions takes place, and to arrive at a general expression for the action of chlorhydric sulphate on organic bodies.

Action of $SO_2.HO.Cl$ *on Bromobenzene*, C_6H_5Br.

Monobromobenzene, 1 eq., diluted with carbonic disulphide, was mixed with the chloride, 1 eq.; moderate reaction took place, hydrochloric acid being evolved in quantity. After warming on the water-bath for a short time, the carbonic disulphide was distilled off, and the product mixed with water. A brownish, semi-solid mass then separated out, and was removed by filtration; the filtrate was neutralised by baryta-water, and heated to boiling, whilst a current of carbonic anhydride was passed into it, to remove excess of baryta. On cooling, a difficultly soluble barium salt crystallised out in magnificent, white, iridescent plates, which were pressed and dried between bibulous paper and analysed.

* Zeitschrift für Chemie, 1869, 41.

1·4032 grm. lost ·035 grm. on drying at 100° = 8·6 per cent. OH_2.

·4494 grm. dry salt gave ·1723 grm. $BaSO_4$ = 22·5 per cent. Ba.

These numbers correspond well with the formula $(C_6H_4BrSO_3)_2Ba$ + 3 aq., which requires 8·1 per cent. OH_2, and 22·6 per cent. Ba.

The portion insoluble in water was washed with cold alcohol, to free it from adhering bromobenzene, and then dissolved in hot alcohol; on cooling, it crystallised in fine, long, white, glistening needles, which, after pressing and drying at 100°, were analysed with the following results:—

·4271 grm. gave ·607 grm. CO_2 and ·0974 grm. OH_2 = 38·7 per cent. C., and 2·5 per cent. H.

The formula $\begin{matrix}C_6H_4Br\\C_6H_4Br\end{matrix}SO_2$—dibromosulphobenzide—requires 38·3 per cent. C., and 2·1 per cent. H. When dry, this body forms white, silky needles, soluble in hot, difficultly soluble in cold alcohol. It melts at 168° and solidifies again at 149°.

The action on bromobenzene is, therefore, somewhat different to that on benzene. Bromosulphobenzolic acid is the main product, the yield of dibromosulphobenzide not exceeding 20 per cent. Bromosulphobenzolic chloride was formed, if at all, in but very small quantity.

Whether the bromosulphobenzolic acid thus obtained is identical with that prepared by the action of concentrated sulphuric acid on bromobenzene, I cannot state, not having compared them directly.

Action of $SO_2.HO.Cl$ *on Nitrobenzene*, $C_6H_5NO_2$.

The two bodies were mixed, as before, in the proportion of 1 eq. of each, but without the addition of carbonic disulphide. In this case the action was extremely sluggish, and it was only after long-continued warming that the evolution of hydrochloric acid ceased. On mixing with water, a small quantity of a black, tarry mass remained, which may *possibly* contain dinitrosulphobenzide. The solution was converted into the barium salt, but as this was exceedingly impure, it was dissolved, together with a quantity of baric hydrate, and the solution saturated with hydrogen sulphide. After boiling the solution, the barium was carefully precipitated by sulphuric acid, and the filtrate evaporated to crystallisation. By this means the very impure nitrosulphobenzolic acid first formed was reduced to the amido-acid, which could more easily be purified.

According to Schmitt,* by the action of concentrated sulphuric acid

* Ann. Ch. Pharm., cxx, 163.

on nitrobenzene and reduction of the product to the amido-acid, an amido-sulphobenzolic acid, is obtained, isomeric with sulphanilic acid prepared from concentrated sulphuric acid and amidobenzene (aniline). His acid crystallises with $1\frac{1}{2}$ mol. aq.; sulphanilic acid with 1 mol. only. My product, I believe, is not sulphanilic acid, being much too soluble in water, and crystallising differently; but, on the other hand, it crystallises with only 1 mol. aq.:—

1·2555 grm. lost ·1153 grm. = 9·1 per cent. OH_2.
$C_6H_4NH_2.HSO_3$ + aq. requires 9·4 per cent.,

so that, until it has been compared directly with Schmitt's acid, it is impossible to say with certainty whether, by the action of sulphuric acid and of chlorhydric sulphate on nitrobenzene, the same or isomeric sulpho-acids are produced.

Action of $SO_2.HO.Cl$ *on Nitrophenol*, $C_6H_4NO_2.HO$.

Nitrophenol (the volatile modification, melting point 45°) 1 eq., suspended in carbonic disulphide was mixed with 1 eq. of the chloride, immediate action took place, and large quantities of hydrochloric acid were evolved. After distilling off the carbonic disulphide, the product was *entirely* soluble in water.

The excess of sulphuric acid was removed by lead carbonate, the excess of lead by hydrogen sulphide, and the solution was then neutralised with potassic carbonate, and evaporated to crystallisation. In this way the very characteristic yellow needles of the *dipotassic nitrophenolsulphate*, $C_6H_3NO_2.OK.SO_3K$ + 2 aq. were obtained, and from a solution of this salt, on the addition of acetic acid, the tufts of light-yellow needles of *potassic nitrophenolsulphate*, $C_6H_3NO_2.OH.SO_3K$.

Very remarkable is the action of the chloride on the non-volatile modification of nitrophenol. According to Kekulé, whereas the volatile modification is readily converted into the sulpho-acid by the action of concentrated sulphuric acid, it is not possible to prepare a sulphoacid from the isomeric, non-volatile modification. The same nitro-acid was prepared by Kolbe and Gauhe, by nitration of para-phenolsulphonic acid; they could not, however, obtain a nitro-acid by the action of nitric acid on metaphenolsulphonic acid. I had hoped to obtain such an acid by the action of $SO_2.HO.Cl$, but it is not so.

When these substances are mixed in equivalent proportions, with the addition of carbonic disulphide, immediate action takes place, and large quantities of hydrochloric acid are evolved. On the addition of water, an oil separated, which dissolved almost entirely in hot water, but from the solution on cooling the characteristic long, white needles of nitrophenol crystallised out; the filtrate contained only sulphuric acid and traces of nitrophenol.

The sulpho-acid, if formed (and it seems to me beyond doubt that it is) in the first instance, is evidently decomposed by water into nitrophenol and sulphuric acid.

It may, perhaps, be possible to isolate it by appropriate treatment.

Action of $SO_2.HO.Cl$ *on Naphthalene.*

1 eq. naphthalene dissolved in carbonic disulphide, was acted on by 1 eq. chlorhydric sulphate; violent action took place, accompanied by evolution of hydrochloric acid. The reaction was terminated, after distilling off the carbonic disulphide, by heating for some time at 100°. The residue remaining after treatment of the product with water, consisted almost entirely of naphthalene, since it was volatilised on boiling with water. The naphthalene compound analogous to sulphobenzide, is, therefore, not formed in any appreciable quantity. From the aqueous solution a barium salt was obtained, containing 24·4 per cent. of barium. Baric sulphonaphthalate requires 24·7.

To decide, if possible, whether both the α and β modifications of sulphonaphthalic acid were formed, the calcium salt was prepared, and a determination of the water of crystallisation made. The β-salt is anhydrous, whereas the α-salt crystallises with 2 mols. aq., corresponding to 7·3 per cent; my salt contained 3·6 per cent., and, I believe, therefore, was a mixture of the two isomeric salts. In all probability, the α-acid first formed is converted by subsequent heating into β-acid. The anhydrous calcium salt contained 8·8 per cent. Ca; required 8 per cent.

By the action of 2 mols. $SO_2.HO.Cl$ on 1 mol. naphthalene, a *disulpho-acid* is formed.

The conclusion to be drawn from the above few experiments is, it seems to me, that the normal action, so to speak, of chlorhydric sulphate, is to form a *sulpho-acid*, the chlorine of the chloride removing hydrogen from the body acted upon and replacing it by the group SO_3H; it is only under certain conditions that both Cl and HO are removed from the chloride, and a compound analogous to sulphobenzide is formed. What these conditions are, I hope to establish by a further more extended series of experiments.

XV.—*On a Water from the Coal Measures at Westville, Nova Scotia.*

By Professor How, D.C.L., University of King's College, Windsor, N.S.

In a paper published in the Journal of the Chemical Society for May 1870, I described an acid water from the Acadia Coal Mines at Stellar-

ton, Picton county, N.S. The subject of the present communication was obtained from a neighbouring mine in the same county, the Black Diamond Colliery, situated at Westville, a new village about two miles west of the former place. This water differs from that obtained at Stellarton, which was partly of surface origin, in having been taken from a coal pit, and while the former furnished a good illustration of the evils attending the use of such a water in boilers, this gives an opportunity of comparing a water from the productive coal measures with those arising under different geological conditions. In 1865, I described to the Society* a dense brine from Salt-springs, Picton county, which, though containing more salt than the others, as yet ascertained, probably shows the general character of the brines issuing from the lower carboniferous and gypsiferous districts of this province, since it agrees with another of them, from Walton, a distant locality, as I have shown,† in containing sulphate of calcium as the most abundant ingredient after chloride of sodium, and smaller quantities of chloride and carbonate of magnesium and calcium, though the amounts of these are not alike, either absolutely or relatively, There are other waters arising in these gypsiferous districts in which sulphates are the chief constituents, chlorides being nearly absent. For example, the Spa Spring water of Windsor, Hants county, contained, when I analysed it in 1858, solid matter to the amount of 138 grains in the imperial gallon, of which about 106 were sulphate of calcium, 12 consisted of sulphates of magnesium, sodium and potassium, and only 0·9 of any chloride, that of sodium.‡ These eminently sulphated waters present interesting contrasts with those in which chlorides are by much the preponderating constituents, as the saline water of Bras d'Or, Cape Breton, analysed by myself,§ the brines of Onondaga, New York, examined by Professor Gössmann,‖ several others described by Dr. Hunt,¶ and the Wheal Clifford water analysed by Professor W. A. Miller,** and also with the Kissingen water at Harrogate, examined by Dr. S. Muspratt,†† and those described by Dr. Hunt,‡‡ in which chlorides are abundant and sulphates are absent. All these waters, excepting that from Harrogate, which is from rocks at the junction of the permian with the carboniferous, issue from systems older than the carboniferous; and we see the same features presented by waters of intermediate times: for the brines of the valley of the Alleghany River, obtained from borings in the coal formation, are remarkable for containing large proportions of

* Journal of the Chemical Society, xviii, 44.

† Transactions N.S. Institute, 1865, and Mineralogy of N.S., p. 143.

‡ Chem. News, ix, 98.

§ Chem. News, ix, 97.

‖ Silliman's Journal, July, 1867.

¶ Geology of Canada, 1863, p. 53; and Contributions to the Chemistry of Waters Silliman's Journal, 1865.

** Chem. News, x, 181.

†† Chem. News, xiv, 49, and xv, 245.

‡‡ Loc. cit.

chlorides of calcium and magnesium, though the sum of these is never equal to more than about one-fourth of the chloride of sodium. The presence of salts of barium and strontium in these brines, and the consequent absence of sulphates, is, according to Lenny, a constant character in this region over an area of two thousand square miles.* In this curious circumstance, these waters agree with the Kissingen water, and several of the Canadian waters described by Dr. Hunt.†

The water now to be described was mentioned as having been taken from the productive coal measures. These constitute the middle coal formation or the coal measures proper of this province, according to the arrangement of Dr. Dawson, who says that this series includes the productive beds of coal, and is destitute of true marine limestones. Beds tinged with peroxide of iron, are less common in this formation than in any of the others of the system. Dark-coloured shales and grey sandstones prevail, and there are no conglomerates.‡ These beds are separated from the gypsiferous group before referred to by the underlying millstone grit series, and they represent the lower coal measures of the United States, and in part, the coal formation of Britain.

Two samples of water were taken from the same pit at the Black Diamond Colliery, under somewhat different circumstances, and sent to me for examination in November 1870, by A. W. Greig Esq., superintendent of the Nova Scotia Coal Company, who was desirous of ascertaining whether the water would answer for use in his boilers. The waters were bright and clear; they had no odour; their taste was that of good spring water. They gave respectively the following results:—

	Grains in the imperial gallon.	
	No. 1.	No. 2.
Silica	0·63	0·46
Carbonate of calcium	11·55	10·59
Carbonate of magnesium	3·67	3·57
Carbonate of iron	traces	traces
Chloride of sodium	0·84	1·17
Sulphate of potassium	1·14	1·58
Sulphate of sodium	4·17	2·50
Phosphoric acid	none	none
Organic matter	none	traces
Carbonate of sodium	3·55	3·35
	25·55	23·22
Free carbonic acid	undet.	undet.
Specific gravity	1000·459	1000·339

* Bischof, Chemical Geology, i, 377. † Loc cit.
‡ Acadian Geology, Second Edition, p. 130.

Hence it appears that the waters were essentially the same; they had an acid reaction on litmus; the paper regained its blue colour on drying; they gave off a good deal of carbonic acid gas, and deposited carbonates of calcium and magnesium on boiling; nearly all the former was thrown down after two or three hours' boiling, and on concentration, a mere trace remained dissolved. The waters soon acquired an alkaline reaction on evaporation; and when concentrated, they coloured turmeric deep brown, effervesced with acids, and contained sulphates, alkalies, and a notable quantity of magnesia.

The waters being one and the same, may be spoken of as the water from Westville, and, of course, in reference to the condition after loss of the carbonic acid, which renders the carbonates present bicarbonates, as an alkaline water. It is interesting to find the composition of this water so totally unlike that of any of the waters of this province as yet analysed, though this was to be expected considering the different geological conditions under which those which have been examined arise. The small quantity of chlorides may have some relation to the absence of marine limestones in the productive measures mentioned by Dr. Dawson, and is in very strong contrast with that in the brines from the coal-formation of the Alleghany River district referred to above. In the waters containing carbonate of sodium analysed by Dr. Hunt, which form his fourth class,* chlorides are sometimes absolutely and relatively more abundant than in this case; but on the whole, this is the class to which the Westville or Black Diamond Colliery water belongs.

* Loc. cit.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

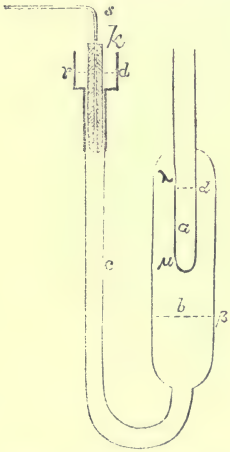
Physical Chemistry.

Calorimetric Researches. By R. BUNSEN.*

BUNSEN has devised a new method of calorimetry, which is applicable to small quantities of material, and thus facilitates the estimation of the specific heat of rare substances.

The instrument he uses consists of a glass vessel *a*, in the form of a common test-tube, fused into a vessel *b*, which terminates in the bent tube *c*. Into the upper extremity of this tube a graduated tube *s* of small calibre is inserted, and luted with fine sealing-wax into a cork, *k*. An iron collar, *d*, serves the double purpose of containing mercury to render the joint perfect, and affording the means of clamping the instrument to a firm support.

The inner vessel *a* is filled with boiled water from μ to α, as also is the outer vessel from β to λ. The rest of the apparatus from β to γ is filled with boiled mercury.



A cylinder of ice is formed in the vessel *b* by surrounding the whole instrument with snow. When the water congeals, the mercury is driven out through the tube *c*. The scale-tube, *s*, is inserted into its place, and the mercury-thread adjusted to the desired position either by depressing the cork, or in a manner which will be described later. The substance to be examined, after it has been heated sufficiently and its temperature noted,† is allowed to drop into the water in the tube *a*. In the bottom of this tube a piece of cotton wool is placed and kept in position by means of a piece of platinum wire coiled round it. This prevents breakage, and facilitates the extraction of the substance after the operation is completed. The tube *a* is closed with a cork, to prevent change of air.

When the heated body under examination is introduced into the vessel *a*, some of the surrounding ice is melted, and the volume

* Phil. Mag. [4], xli, 161; from Pogg. Ann., cxli, 1.

† Bunsen has devised an admirable method for effecting this accurately.

becomes less. The mercury below rises, and indicates its rise by the retraction in the graduated tube s. For relative measurements of the amount of heat given up by substances, it is sufficient to observe the number of divisions through which the mercury is drawn back. To convert these readings into thermal units, they must be multiplied by a constant obtained by the following considerations :—

Let T = a number of calibrated divisions of the scale tube; t = temperature of the mercury contained in T; g = the weight of the thread of mercury, T, in grms.; m = specific gravity of mercury at 0° C.; α = its co-efficient of expansion. Then we have for the capacity of one division of the tube in cubic centimetres—

$$v = \frac{g\,(1 + \alpha)}{m\mathrm{T}} \qquad (1)$$

In Bunsen's apparatus, v = 0·00007733 cc.

Let i = specific gravity of ice at 0° C.; w = specific gravity of water at 0° C.; p = weight of ice such that the change of volume due to its melting draws the mercury over one division of the scale having a volume v; then v = difference of volume of p of ice at 0° C., and p of water at 0° C., or $v = \frac{p}{i} - \frac{p}{w}$.

This gives $\frac{v\,i\,w}{w - i} = p$. (2)

Bunsen found it necessary to redetermine the specific gravity of ice, as the observations of other inquirers showed a want of agreement. This he did with his wonted ingenuity. The number he obtained for i was 0·91674. Using this number, and adopting the commonly received specific gravity of water at 0° C., namely 0·99988, the constant p in his instrument had the value 0·00085257.

The weight of melted ice (W) in grammes corresponding to T corrected divisions on the scale is therefore—

$$\mathrm{W} = 0{\cdot}00085257\ \mathrm{T} \qquad (3)$$

Let l = latent heat of liquidity of water, then pl = the quantity of heat corresponding to one scale-division.

For the amount of heat, H, expressed in units of heat, which T scale-divisions indicate, we have—

$$\mathrm{H} = pl\,\mathrm{T}$$

or, when we take for l the value 80·025, then

$$\mathrm{H} = 0{\cdot}068227\ \mathrm{T} \qquad (4)$$

The delicacy of the instrument is well illustrated by one of the methods used to bring the thread of mercury to a desired point on the scale-tube. A small brass weight tied to a thread was warmed in the

hand, or by placing it under the tongue, and then held in the water *a*. On dipping 0·4 grms. of brass, at 37° C., into 20 grms. of water at 0°, a thermometer only indicated 0·07° C.; in the calorimeter, however, the mercury was drawn back through no less than 20 mm. divisions of the scale. It will be seen, too, that all the heat given up by the substance is used to melt the ice, and none is lost, as in other calorimeters. The ice cylinder formed in *b* can be used for a week, provided care be taken to renew the surrounding snow night and morning. If the instrument is employed to measure the specific heat of liquids, the liquid is enclosed in a glass tube weighted with platinum. In this case the corrections for the glass and platinum must be made. Bunsen has not yet determined latent heats of liquidity in his instrument, as the winter has not been suitable for such experiments. He thinks it will be possible, with the ice-calorimeter, to determine the heat of gaseous combustion with greater accuracy than by former methods, as small quantities only need be used, which can easily be prepared in a pure state.

Bunsen has determined by his new method the specific heats of several pure elements not hitherto examined. The results are given in Table I, together with the atomic heats of the same elements.

TABLE I.

Elements.	Specific heat. *a*.	Atomic weight. *b*.	Atomic heat. *a* × *b*.
Ruthenium	0·0611	52·0	3·18
Calcium	0·1722	20·0	3·44
Calcium	0·1618	20·0	3·37
Allotropic tin	0·0545	58·8	3·21
Cast tin	0·0559	58·8	3·39
Indium	0·0574	37·8	2·17
Indium	0·0565	37·8	2·33

In the case of indium, it will be seen that the atomic heat is below the ordinary value. If the atomic weight, however, be taken as one and a half times 37·92,* we shall have In = 56·7, which, multiplied by the specific heat, as determined, gives 3·23 for its atomic heat, a close approximation to that of the other elements. If this view be received, indium in indic oxide must be looked upon as trivalent, and the formulæ in column II must be substituted for those in column I, Table II.

* This is Bunsen's new determination.

TABLE II.

	I.	II.
Black indous oxide	In_2O ?	InO ?
Yellow indic oxide	InO	In_2O_3
Green oxide of indium	$5InO.In_2O$	$2InO.In_2O_3$
Grey oxide of indium	$4InO.In_2O$	$3InO.2In_2O_3$
Indic hydrate.....	InO.HO	$In_2O_3.3HO$
Indic sulphate	$InO.SO_3.3HO$	$In_2O_3.3SO_3.2HO$
Indic chloride.....	InCl	In_2Cl_3
Ammonio-indic chloride {	$2NH_4Cl.3InCl$ 2HO	$2NH_4Cl.In_2Cl_3$, 2HO.

S. W.

On the Relation of the Chemical Constitution to the Refractive Power of Gases. By F. MOHR.*

THE author takes the refractive indices of simple and compound gases, as determined by Dulong, and divides them by the specific gravity. This he terms their chemical refractive power. On comparing the numbers he observes that hydrogen is by far the highest, and that its presence in a compound raises its refractive power, while oxygen is the lowest in the list, and its presence depresses the refraction. He treats the refractive indices of several fluid and solid bodies in a similar way with a similar result, and enters on speculative considerations with reference to combustibility.

R. S.

Optical Arguments on the Nature of Water of Hydration. By F. MOHR.†

IN this paper the author takes the refractive indices of certain isomeric groups of organic bodies, as determined by Landolt, and divides them also by the specific gravity. He shows that these "reduced indices" of the hydrated acids (such as propionic acid, $C_6H_5O_3,HO$) are always lower than those of the isomeric ethers (such as methylic acetate, or ethylic formate, $C_6H_6O_4$), while the specific gravities and boiling points are higher. He attributes this to the different manner of combination of the hydrogen in the two cases. R. S.

On the Constant Colour and Intensity of the Light from Clouds, for Chromometry. By A. MÜLLER.‡

THE object of this paper is to point out the similarity of the colour of

* Deut. Chem. Ges. Ber. iv, 149. †*Ibid.* 154. ‡ *Ibid.* 105.

direct sunlight, and of light reflected from clouds. The method adopted was by having two standard solutions, one of cuprammonia, and the other an acid solution of ferric acetate, and comparing the combined tints of different lengths of the two solutions with a complementary glass plate. It was found that the proportional lengths of the blue and yellow solutions remained practically the same, whether the light used was from clouds or direct sunlight. A. P.

On the Various Tints of Autumnal Foliage. By H. C. Sorby.*

In investigating the numerous colouring principles which exist in leaves, chemical analysis is of little use; the micro-spectroscope, however, furnishes a method of testing which is specially useful, because particular substances can be recognised in mixtures without the necessity of obtaining them in a separate state. The colouring matters in leaves may be separated into five distinct groups, each of which consists of many species nearly related to each other. It is proposed to call these groups *Chlorophyll*, *Xanthophyll*, *Erythrophyll*, *Chrysophyll*, and *Phaiophyll*; the first two, generally speaking, are insoluble in water, but soluble in alcohol and in bisulphide of carbon; the last three are soluble in water and aqueous alcohol, but insoluble in bisulphide of carbon.

Chlorophyll has been considered as a single substance, but optical examination has proved the existence of a number of separate species. The prevailing tint of this group is a deep green, and its absorption spectrum is characterised by a well-marked absorption-band in the red, the green and blue being more or less completely transmitted.

The *Xanthophyll* colouring matters have a bright yellow colour; the spectra show absorption at the blue end, the remaining colours from the red to the yellow-green pass freely. The group of colours called *Erythrophyll* are crimson-red, and give a strong absorption in the green. When slightly oxidized, the colour becomes orange-yellow, but on further oxidation it seems to be entirely destroyed.

Chrysophyll colours are golden-yellow, but do not possess any remarkable absorption spectra; they are oxidized to pink substances by the action of potassic nitrate and hydrochloric acid. These pink-red substances, when kept for some time in the dry state, or when acted on by ammonia, are modified into various brown substances, some of them having a remarkable resemblance to the phaiophyll colours.

The *Phaiophyll* group consists of the various browns, which are probably due in most cases to the oxidation of chrysophyll colours; a subdivision might be made here by placing the lighter browns in the phaiophyll group, and including the dark browns and blacks under the head of Humus.

* Chemical News, xxiii, 137.

Leaves generally contain colours belonging to several groups, and frequently more than one of the same group. Green leaves are coloured mainly by chlorophyll, the tint of which is modified by the presence of members of the xanthophyll and chrysophyll groups. If erythrophyll is contained in leaves to any extent, they are very much darkened, the chlorophyll absorbing the red and blue of the spectrum, whilst the erythrophyll absorbs the green.

The change of colour which takes place in autumn consists chiefly in the disappearance of the chlorophyll, rendering the remaining colours visible; most frequently these are yellow. It was found with leaves which turn red, that by diminishing the vital power of the plants, the intensity of the colour was increased.

Chrysophyll and chlorophyll may on the whole be considered characteristic of the complete vitality and growth of leaves, erythrophyll and xanthophyll of low vitality and change, and phaiophyll and humus of death and decomposition.

A. P.

On the Absorption-spectrum of Liquid Nitrogen Tetroxide. By AUG. KUNDT.*

To the present time it has been accepted that the broad absorption-bands of liquid hyponitric acid have no connection with the absorption lines of the gaseous acid. The author compared the two spectra by bringing the plane of demarcation between liquid and gas contained in a $\frac{3}{4}$-inch tube before the slit of a spectrum apparatus. The line-groups corresponded with the bands. On cooling the liquid, those in the green, and on warming, those in the red part of the spectrum became more marked.

C. H. G.

On the Reversal of the Sodium Line. By A. WEINHOLD.†

THE ordinary method for obtaining the reversal of the sodium line is to bring a flame coloured with sodium vapour, between the slit of the spectroscope and a powerful white light, such as the lime light. The process described is more simple, and consists in using a petroleum lamp as the source of the continuous spectrum; a slit, without collimating lens, and a powerful prism, forming the spectroscope, no observing telescope being used. The dark sodium line is produced by interposing between the prism and the eye a spirit-lamp flame, intensely coloured yellow by sodic chloride, so as to cover the entire spectrum.

* Zeitschr. f. Chem. [2], vii, 64, from Pogg. Ann., cxli, 157.

† Pogg. Ann., cxlii, 32.

If, however, the sodium flame be placed in front of the slit, the bright yellow line is immediately visible on the continuous spectrum.

The use of an ordinary spectroscope with its telescopes did not give a good result. When the sodium flame was interposed between the prism and the observing telescope, the image was much twisted by the current of hot air, while the construction of the spectroscope does not admit of the flame being placed close behind the slit, or between the eye-piece and the objective. A. P.

On the Electrolysis of some Chemical Combinations. By N. BUNGE.*

AN alcoholic solution of sodium phenylmercaptan (water decomposes this compound) gave by electrolysis, at the negative pole, hydrogen and sodium hydrate; at the positive, a crystalline substance, which on analysis proved to be phenyl bisulphide. The aqueous solutions of sodium ethylmercaptan and sodium amylmercaptan behaved in a similar manner. Hydrosulphuric acid and potassium sulphide, on the electrolysis of their aqueous solutions, gave hydrogen at the negative pole, and sulphur and sulphuretted hydrogen at the positive pole. The aqueous solutions of potassium sulphobenzoate and isethionate gave, by electrolysis, hydrogen at the negative pole, and at the positive principally oxygen and the free acid.

C. E. G.

A Lecture Experiment in Illustration of Gaseous Diffusion. By F. WÖHLER.†

THE author cements a porous galvanic battery cell on the end of a glass tube. The tube being filled with hydrogen, the end is dipped into water, which immediately rises in the tube; or the tube containing air is supported over a trough of water into which the end dips, and a glass bell is inverted over the porous cell and filled with hydrogen; air immediately bubbles out of the tube, the bell is removed, and the water rises rapidly.

F. H. H.

Lecture Apparatus for Condensing Ammonia. By F. C. G. MÜLLER.‡

A STRONG glass tube of 16 millim. diameter is bent twice at right angles in U-form and sealed at each end, the one leg being 10, the other 38 centim. long; a narrow tube furnished with a stop-cock connects the two legs a little below the bends; mid-way between the junction

* Zeitschr. f. Chem. [2], vii, 58, from Deut. Chem. Ges. Ber., iii, 911.

† Deut. Chem. Ges. Ber. iv, 10.

‡ Ann. Ch. Pharm. clvii, 348.

with this connecting tube and the bend of the longer limb, a tube of 1 millim. diameter is joined to the continuation of the shorter limb and to the longer limb passing down inside the latter to its extremity. The longer limb is then three-quarters filled with a saturated solution of ammonia in absolute alcohol, care being taken to expel all the air from the apparatus. The longer limb is then adjusted by a cork in a cylinder in connection with a vessel arranged to inject steam into the cylinder, which is three-quarters filled with a solution of common salt. The shorter limb is immersed in a cylinder filled with ice and water. Steam is now driven into the cylinder and stop-cock is opened: at 90° the first drops of ammonia collect in the short leg, and at 100° the gas passes over rapidly. The pressure in the apparatus does not exceed six atmospheres, and under this pressure the boiling point of alcohol is not far from 100°. As the boiling point of water under these conditions would be about 130°, an aqueous solution of ammonia would not be appropriate. The experiment requires about half an hour for completion.

The reabsorption of the gas is effected by the aid of the connecting tube carrying a stop-cock, and the narrow tube passing through the alcohol, and in the following manner: The water surrounding the longer limb is gradually cooled, the stop-cock is closed, and the ice removed from the short leg, whereupon the gas filling the space above the alcohol is absorbed by the latter; a proportional amount of pressure being thus taken off, the liquid ammonia in the short leg volatilises and rushes through the bends and the narrow tube into the alcohol, which it agitates violently, causing thorough mixing of the strong and dilute solutions. This operation which, in the absence of the narrow tube, would take a very long time to be completed, owing to the surface of alcohol exposed, and the lightness of the saturated alcoholic solution of ammonia, is by its means very quickly finished.

The experiment may of course be repeated as often as desired.

F. H. H.

Inorganic Chemistry.

Lecture Experiments. By V. Wartha.*

Reversed Flames.—An ordinary cylinder, as used in paraffin lamps, is closed below by a doubly perforated cork. One perforation carries a glass tube 2 to 3 mm. diameter, the other, at a distance of 5—6 mm., holds a brass tube, a cork-borer for example, of 12 mm. diameter. The glass tube is brought into communication with the gas supply, the

* Deut. Chem. Ges. Ber., iv, 91.

cylinder is removed, the gas lighted, and the flame regulated to a length of 2 or 3 inches. The cylinder is now replaced and the gas turned on fully. The gas flame will now be extinguished, but the air drawn in through the brass tube will burn with a slightly luminous flame, the size of which may be regulated by partially closing the lower opening of the brass tube. The excess of gas issuing from the upper opening of the cylinder (which should have a strip of sheet copper wound round it) may next be lighted, when the ordinary and the reversed flame will be seen together. On slowly turning down the gas, the air flame is extinguished, and the gas flame rekindled; these phenomena may be repeated at will. For the perfect success of the experiment it is absolutely necessary to keep to the exact dimensions given, and to have the opening of the glass tube bent slightly towards the brass tube, and about 12 mm. from the upper rim of it. When the air flame is burning, we may, in addition, pass a narrow glass tube, also in connection with the gas supply, up the brass tube; we can thus get a small gas jet inside the air flame. By impregnating pieces of flannel with various salts, and after drying, knocking the dust out of them below the brass tube, a variety of colours may be imparted to the air flame.

Decrease and Increase of Weight produced by successive Reduction and Oxidation.—A glass rod and platinum wire, with cylinder of cupric oxide, prepared according to the directions of Thomsen,* are fixed to one end of the beam of a balance, which is then brought into equilibrium. The cylinder, without being detached, is placed for a short time in the luminous flame of a triple-jet Bunsen's burner; when the cylinder has become heated the flame is extinguished, and the gas itself allowed to play against it. The cupric oxide, which will continue to glow, becomes reduced, and the equilibrium of the balance is, of course, disturbed. If then the burner is again lighted, air being this time admitted, the oxidizing flame thus produced will speedily reoxidize the copper, and the equilibrium of the balance will be restored. The phenomena may be repeated as often as desired.

Burning Magnesium in Carbon Dioxide.—An ordinary soda-water syphon is fixed upside down to a retort stand. The delivery tube is connected by caoutchouc tubing with a glass tube, which, by means of a perforated cork, is fixed in the lower opening of an upright ordinary argand glass chimney. By pressing the handle of the syphon carbon dioxide can be admitted at will into this cylinder. The ignited magnesium wire is passed in and repeatedly knocked against the sides of the glass. Considerable quantities of magnesia and carbon are deposited on the glass, and the carbon is easily seen without the use of hydrochloric acid. A. D.

* Deut. Chem. Ges. Ber. iii. 932.

On the Metallammonias or Metallammines. By C. W. BLOMSTRAND.*

IN a former paper† the author has expressed the view that the double salts of cyanogen, and the double and triple salts of nitrous acid, as well as the metallammonias, may be conjugated compounds of pentatomic nitrogen. The interesting researches of P. F. Cleve on the platinum ammonias, and the views published by Dr. Odling on the ammonia compounds of platinum, have caused him to return to the subject.

The fact of the uniform rise in atomic value of the elements by even numbers of bonds (Angriffspunkte) renders it very evident that the bonds of a diad or triad element, for example, cannot be entirely similar to those which become active with its rise to the tetra- or pentatomic state. Bearing in mind that the elements generally act as radicals only in their lower states of combination, the higher bonds may be called *extra-radical bonds*. Three or more atoms being united in a series, it will be seen that outwardly acting extra-radical bonds will still be preserved.

The capability of being polymerized, so to speak, is possessed by different elements in a different degree, but by none to so great an extent as by carbon. With pentatomic nitrogen and other elements this capability appears to be influenced by certain external conditions. Thus, with at least extremely rare exceptions, nitrogen appears to require to be united to a metal which, in some sort, serves as the foundation of the whole. The metallammonias are the only certainly known examples of this kind of nitrogen-compound. With an organic radical in place of the metal, the ammonia appears never to double itself. It is also remarkable that with the metallammonias the externally acting ammonium is with far more difficulty converted into a freely acting triatomic ammonia than with the organic ammonias.

The special importance of the metal as the primary radical of the whole compound is also shown by the fact that the nature of the metal appears to determine, not only the greater or lesser stability of the entire combination, but also the greatest number of nitrogen atoms that can be, and usually are, united with it. Thus Cu and Pt can bind together at the most two atoms of nitrogen, while Ni, Co, Ir, and Rh can cause three atoms to unite together, as in—

$$Pt\begin{matrix}NH_3.NH_3.Cl\\NH_3.NH_3.Cl\end{matrix} \text{ and } Co\begin{matrix}NH_3.NH_3.NH_3.Cl\\NH_3.NH_3.NH_3.Cl\end{matrix}$$

That the *intra-radical bonds* may at the same time also take part in this union of atom to atom of an element, is shown by the fact that

* Deut. Chem. Ges. Ber., iv, 40.

† Ibid., ii, 202.

some elements in their lowest combining state present themselves with two or more atoms acting in common, as the mercury, Hg″.Hg″, in mercurous chloride, the sulphur in the polysulphides and polythionic acids, etc. The double union of carbon in the aromatic series, of tri-atomic nitrogen in azobenzide and bodies allied to it, and of tri- and pentatomic nitrogen in azoxybenzide, as well as, according to the author's ideas, of chlorine in the haloïd double salts, and of pentatomic nitrogen in the cyanogen and nitroxyl double salts, may be examples of this somewhat anomalous, but certainly not rare, mode of union.

The intra-radical bonds may also in some cases serve singly for such unions, as frequently occurs in carbon radicals, and of which the numerous isomeric bodies are examples. It is also superabundantly proved that carbon radicals can in the same way enter into the interior, as it were, of ammonia. But it is very doubtful whether nitrogen acting pentatomically can in a similar manner fix nitrogen.

$H.CH_2.H$ is easily obtainable and very stable; so is $H.CH_2.CH_2.H$, etc. The chlorinated bodies $H.CH_2.Cl$ and $H.CH_2.CH_2.Cl$, etc., are somewhat difficult to bring into double decomposition, but yet they act in every respect as chlorine-compounds of independent radicals, CH_3 and C_2H_5.

On the other hand, the nitro-hydrogen, $H.NH_3.H$, not to mention the more complex ones, does not exist. The NH_4 in $H.NH_3.Cl$ shows so decidedly the characteristics of a radical as to rival in this respect the alkali-metals. In other words, with these, as with other polyatomic elements, the extra-radical bonds behave as electro-chemically different, but far more so with nitrogen than with carbon.

From this, therefore, it appears to the author that, while methyl replaces quite normally the hydrogen in methyl, CH_3, or in methylene, CH_2, a replacement of the hydrogen of ammonia, NH_3, or of ammonium, NH_4, by ammonium must, on the face of things, be impossible. The fifth bond of pentatomic nitrogen, united with hydrogen, occupies a decidedly negative position.

Hence the particular faultiness of the older formulæ for Reiset's first base—in which ammonium is taken as the substitute for hydrogen in ammonium—such as that of Kolbe, long generally accepted, and that of Frankland :—

Kolbe.

$$\left.\begin{matrix} H_2 \\ H_4N \\ Pt \end{matrix}\right\} N.Cl.$$

Frankland.

$$Pt\begin{matrix} NH_2(NH_4)Cl \\ NH_2(NH_4)Cl \end{matrix}$$

Much more accurate is Kolbe's more recent formula*—

$$\left.\begin{matrix} [Pt(H_3N)_2]'' \\ H_6 \end{matrix}\right\} N_2Cl_2.$$

* Journ. pr. Chem., 1870, 220.

in which "the radical, $Pt(H_3N)_2$, occupies the place of two atoms of hydrogen in a diammonium dichloride." But typical formulæ like this for the cobalt-bases would be quite unmanageable, and Kolbe gives no atomistic formulæ for these; neither does Odling, whose proposed formulæ for the platinum-ammonias come nearest to the author's, and to a certain extent agree with them. Odling compares the ammonia bases with ethylene, and therefore also recognises as correct the fundamental principles here developed, at least the essential point in them.

But Odling's comparison of $H_2N.H_3N$ or H_5N_2, as the "monad radical ammon-amidogen," with the monad radical methylene-methyl, or ethyl, $H_3C.H_2C$, or H_5C_2, may very easily lead to entirely erroneous notions. In any case H_5N_2 never acts as a monad radical in the same manner as H_5C_2. $H_3N.NH_3$ corresponds to $H_2C.CH_2$: it is useless to go beyond this, because the atomicities still remaining act in an entirely different manner. Further, Odling fully recognises, apparently, that ammonium chloride must be NH_4Cl and not $NH_3.HCl$, and yet where the double ammonia is concerned, he takes the chemically active nitrogen as triatomic, although its pentatomicity is here so decidedly manifested that alkalies hardly ever set free the ammonia, but the hydrated ammonium oxide. Then, too, it must at once be seen that his "amo-diplatinamine" compounds are not diplatinum compounds at all.* The bodies referred to are octatomic, while diplatinum can at the most be regarded as hexatomic so long as there are no grounds for regarding the single atom of platinum as more than tetratomic.

Cleve's researches have, more than any others, thrown light upon the constitution of the platinum bases. The many Pt'''' compounds described by him are of particular interest, as affording the most evident proofs of the influence of place; such, for example, as the sulphato-diammine chloride, not precipitable by barium chloride, which, according to the author's views, may be represented (a standing for NH_3) by

$$Pt\begin{array}{l} O \\ a.a. \\ a.a. \\ O.H. \end{array}\left.\begin{array}{l} \\ \\ \\ \end{array}\right\} SO_2$$

Anderson's pyridine compounds, which seem particularly to support the author's views, may be formulated thus:

Platosopyridine.

$$Pt''\begin{array}{l} N(C_5H_5)'''.Cl \\ N(C_5H_5)'''.Cl \end{array}$$

Platinopyridine.

$$Pt''''\begin{array}{l} Cl \\ N(C_5H_5)'''.Cl \\ N(C_5H_5)'''.Cl \\ Cl. \end{array}$$

* [The author appears here to have misapprehended Dr. Odling's representation of these compounds, in which it is evidently not implied that the two atoms of platinum are associated as a double atom, like Fe_2 and Hg_2 in ferric and mercurous chlorides.—Abs.]

—a triatomic radical being here united to unconditionally pentatomic nitrogen.

Hadow's chloride, Raewsky's nitrochloride, and Gerhardt's nitrate, —represented by Odling as diplatinum compounds, thus:

$$(1)\ Cl_2\quad OPt_2''''(H_5N_2)_4 . 4HCl.$$
$$(2)\ Cl_2\quad OPt_2''''(H_5N_2)_4 . 4HNO_3 . Aq.$$
$$(3)\ (NO_3)_2OPt_2''''(H_5N_2)_4 . 4HNO_3 . Aq.$$

—the author without hesitation (Cleve's researches having proved Hadow's chloride to contain water) writes in this way:

$$(1)\quad Pt''''\begin{matrix} Cl \\ a.a.Cl \\ a.a.Cl \\ O.H. \end{matrix}\qquad (2)\quad Pt''''\begin{matrix} Cl \\ a.a.O.NO_2 \\ a.a.O.NO_2 \\ O.H. \end{matrix}\qquad (3)\quad Pt''''\begin{matrix} O.NO_2 \\ a.a.O.NO_2 \\ a.a.O.NO_2 \\ O.H. \end{matrix}$$

Buckton's double salt, and that of Thomsen, offer highly illustrative examples of the author's views, when represented by atomistic formulæ:

$$Pt\begin{matrix} a.a.Cl.Cl \\ a.a.Cl.Cl \end{matrix}Cu \text{ and } Cu\begin{matrix} a.a.Cl.Cl \\ a.a.Cl.Cl \end{matrix}Pt.$$

Nitrogen joined to nitrogen, and chlorine to chlorine, serve in both cases to connect the whole, but in inverted order. Both are perfectly normal haloïd double salts of different metallammonia bases.

The whole series of platinum bases, with special reference to Cleve's researches, are, as chlorides, thus represented:

(A) Of Platosum, Pt''.

(1) Platodiammine* (Reiset's second base)	$Pt''\begin{matrix} NH_3.NH_3.Cl \\ NH_3.NH_3.Cl. \end{matrix}$
(2) Platosammine (Reiset's first base)	$Pt''\begin{matrix} NH_3.Cl \\ NH_3.Cl. \end{matrix}$
(3) Platosemidiammine	$Pt''\begin{matrix} Cl \\ NH_3.NH_3.Cl. \end{matrix}$

(B) Of Platinicum, Pt''''.

(4) Platindiammine (Gros's base)	$Pt''''\begin{matrix} Cl \\ NH_3.NH_3.Cl \\ NH_3.NH_3.Cl \\ Cl. \end{matrix}$
(5) Platinammine (Gerhardt's base)	$Pt''''\begin{matrix} Cl \\ NH_3.Cl \\ NH_3.Cl \\ Cl. \end{matrix}$

* The termination "ammine" serves to distinguish these bodies from the amines (ethylamine, &c.).

(6) Platinsemidiammine $Pt''''\begin{matrix}Cl\\Cl\\NH_3.NH_3.Cl.\\Cl.\end{matrix}$

(C) Of Diplatinicum, Pt_2^{vi}.

(7) Diplatindiammine $Pt_2^{vi}\begin{matrix}Cl\\NH_3.NH_3.Cl\\NH_3.NH_3.Cl\\NH_3.NH_3.Cl\\NH_3.NH_3.Cl\\Cl.\end{matrix}$

With regard to the cobalt bases, the author finds room for only a few remarks. It appeared to him that luteocobaltia, on account of the ready production of dicobalticum, might be obtained directly from cobaltous triammonia by the action of iodine, according to the equation:

$$\begin{matrix}Co''\begin{matrix}a.a.a.O\\a.a.a.O\end{matrix}SO_2\\Co''\begin{matrix}a.a.a.O\\a.a.a.O\end{matrix}SO_2\end{matrix} + I_2 = \left\{\begin{matrix}I\\Co'''\begin{matrix}a.a.a.O\\a.a.a.O\end{matrix}SO_2\\Co'''\begin{matrix}a.a.a.O\\a.a.a.O\end{matrix}SO_2\\I\end{matrix}\right.$$

a method which would unquestionably be the simplest and most productive yet proposed for obtaining the cobaltic bases. He has found that the salt can thus be obtained and in desirable quantity, the ammoniacal solution of the sulphate being heated for some time with the iodine in atomic proportions. The yellow dicobaltitriammine iodosulphate can be separated without difficulty, on account of its very sparing solubility, from the red dicobaltiditriammine (roseocobaltia) iodosulphate, which is extremely soluble in ammonia.

The author also points out the great stability of the pre-eminently normal luteo-compound, which he is for the most part disposed to regard as a pure triammine-compound, instead of a monoditriammine compound. Thus when the iodosulphate is treated with chlorine, the combined ammonia is not decomposed, nor is the iodine simply separated, but, as in the presence of the true alkalies, some of it remains combined in an oxidized condition.

E. D.

Compounds of Sulphuric Anhydride. By C. Schultz-Sellack.*

The salts corresponding to Nordhausen sulphuric acid have been considered as salts of a peculiar acid, which may be called anhydro-sul-

* Deut. Chem. Ges. Ber., iv, 109.

phuric acid. Only the salts of the alkali metals have been known up to the present time, but Schultz-Sellack has succeeded in preparing the corresponding barium and silver compounds. Other compounds with metals of higher atomicity have been produced, which must be considered as formed by the addition of one molecule of the anhydride to the normal sulphate, whilst in a third class of compounds the sulphuric anhydride acts almost as water of crystallisation.

Anhydro-sulphuric acid, $H_2S_2O_7$, is prepared by mixing the proper quantities of sulphuric acid and liquid sulphuric anhydride, a small excess of the latter being advisable. The crystals obtained are placed under a bell-jar, over sulphuric acid which is not completely concentrated. The pure crystals melt at 35°, and do not give off fumes of sulphuric anhydride at the ordinary temperature.

Potassic anhydro-sulphate, $K_2S_2O_7$, is obtained by heating the normal sulphate with sulphuric anhydride. Jacquelain* has crystallised this body from water, and gives its melting point as 210°. Schultz-Sellack cannot confirm these observations, and places its melting point above 300°.

Hydro-potassic anhydro-sulphate, KHS_2O_7, is obtained by dissolving the preceding salt in strongly fuming sulphuric acid, it crystallises in transparent prisms, which melt at 168°. *Sodic anhydro-sulphate* cannot be obtained quite pure from the solution of the acid salt in fuming acid.

Argentic anhydro-sulphate, $Ag_2S_2O_7$, prepared by dissolving argentic sulphate in fuming acid, giving colourless crystals.

Baric anhydro-sulphate, BaS_2O_7. Crystals of this compound are obtained by heating baric sulphate with fuming acid to 150°. The salt hisses when water is added to it.

Arsenious sulphato-sulphuric anhydride, $As_2(SO_4)_3.SO_3$, is obtained in shining needles by the action of fuming sulphuric acid on arsenious acid. The antimony compound is obtained in small granular crystals by the same method.

Sulphuric anhydride acts on sulphites at 100°, liberating sulphurous anhydride, and producing sulphates; hyposulphites are not formed.

When the chlorides of the alkali-metals are exposed to the long continued action of the vapour of sulphuric anhydride, compounds having nearly the composition $NaCl(SO_3)_4$, and $KCl(SO_3)_8$, are obtained. Silver chloride forms $AgCl(SO_3)_4$, but this is attended with partial decomposition. Baric chloride gives a compound, probably $BaCl_2(SO_3)_2$. On heating these compounds, sulphuric anhydride is first evolved, then chlorine and sulphurous anhydride, and a sulphate is left behind.

Metallic fluorides, *iodides*, and *bromides*, absorb sulphuric anhydride, the two latter with partial decomposition.

* Ann. Ch. Phys., 1870, 311.

Potassic nitrite forms with the anhydride, a compound $KNOSO_4$, which is somewhat analogous to the lead chamber compound.

Selenium forms a compound $SeSO_3$ with the anhydride, whilst *tellurium* is oxidized to a great extent.

Sulphuric anhydride reacts on *sulphur*, producing sulphurous anhydride; with *iodine*, however, it gives laminated crystals, having nearly the composition of I_2SO_3. A. P.

On the Molecular Heat of the Hydrates of Sulphuric Acid, and on their Heat of Combination on mixing them with Water. By L. Pfaundler.*

Interval of temperature from 22° to	Specific heat.			Molecular heat.		
	H_2SO_4.	$H_2SO_4 + H_2O$.	$H_2SO_4 + 2H_2O$.	H_2SO_4.	$H_2SO_4 + H_2O$.	$H_2SO_4 + 2H_2O$.
60°	—	—	0·442	—	—	59·228
70	—	0·444	0·446	—	51·504	59·764
80	0·355	0·447	0·450	34·790	51·852	60·300
90	0·356	0·450	0·455	34·888	52·200	60·970
100	0·358	0·454	0·459	34·084	52·664	61·506
110	0·359	0·458	0·462	35·182	53·128	61·908
120	0·360	0·461	0·466	35·280	53·476	62·444
130	0·362	0·465	0·470	35·476	53·940	62·980
140	0·364	0·469	0·474	35·672	54·404	63·516
150	0·365	0·472	0·478	35·770	54·752	64·032
160	0·367	0·475	0·482	35·966	55·100	64·588
170	0·370	0·479	—	36·260	55·564	—
180	—	0·482	—	—	55·912	—

The following tables give the quantity of heat (in gram-degrees), which is evolved, per molecular weight, on mixing the different hydrates with water:—

I.	H_2SO_4.	with excess of water	17754
	H_2SO_4. H_2O	,, ,, ,,	10921
	H_2SO_4. $2H_2O$	,, ,, ,,	7617
	H_2SO_4. $3H_2O$	,, ,, ,,	6106
	H_2SO_4. $4H_2O$	,, ,, ,,	4844
	H_2SO_4. $5H_2O$	,, ,, ,,	3955
	H_2SO_4. $6H_2O$	,, ,, ,,	3241
	H_2SO_4. $\frac{1}{2}H_2O$	,, ,, ,,	13984
	$H_2SO_4.1\frac{1}{2}H_2O$	,, ,, ,,	9133
	$H_2SO_4.2\frac{1}{2}H_2O$	,, ,, ,,	6729

* Zeitschr. f. Chem. (2), vii, 42.

From these numbers the following tables were calculated:—

H_2SO_4 with	H_2O....	6833		$H_2SO_4.H_2O$ with	H_2O ..	3305
,, ,,	$2H_2O$....	10137		,, ,,	$2H_2O$ ..	4815
,, ,,	$3H_2O$....	11647		,, ,,	$3H_2O$ ..	6077
,, ,,	$4H_2O$....	12910		,, ,,	$4H_2O$ ..	6966
,, ,,	$5H_2O$....	13798		,, ,,	$5H_2O$ ..	7680
,, ,,	$6H_2O$....	14513		,, ,,	excess..	10921
,, ,,	excess ..	17754				

$H_2SO_4.2H_2O$ with	H_2O..	1510	H_2SO_4 with	$H_2SO_4.H_2O$....		708
,, ,,	$2H_2O$..	2772	,, ,, ,,	$.2H_2O$....		3528
,, ,,	$3H_2O$..	3661	,, ,, ,,	$.3H_2O$....		5614
,, ,,	$4H_2O$..	4376	,, ,, ,,	$.4H_2O$....		7365
,, ,,	excess .	7617	,, ,, ,,	$.5H_2O$....		8252

$H_2SO_4.3H_2O$ with	H_2O..	1262	$H_2SO_4.H_2O$ with	$H_2SO_4.2H_2O$		272
,, ,,	$2H_6O$..	2151	,, ,, ,,	$.3H_2O$		1794
,, ,,	$3H_2O$..	2866	,, ,, ,,	$.4H_2O$		2308
,, ,,	excess .	6106	,, ,, ,,	$.5H_2O$		2664

$H_2SO_4.4H_2O$ with	H_2O..	889	$H_2SO_4.2H_2O$ with	$H_2SO.3H_2O$		266
,, ,,	$2H_2O$..	1603	,, ,, ,,	$.4H_2O$		*248
,, ,,	excess .	4844	,, ,, ,,	$.5H_2O$		——
			,, ,, ,,	$.6H_2O$		1169
$H_2SO_4.5H_2O$ with	H_2O ..	714	$H_2SO_4.3H_2O$ with	$H_2SO_4.4H_2O$		——
,, ,,	excess .	3955	,, ,, ,,	$.5H_2O$		373

C. S.

On the Hydrate of Carbon Bisulphide. By M. Ballo.†

The crystalline compound produced by the action of a current of moist air on carbon bisulphide was shown by Berthelot to contain water. Duclaux afterwards gave the crystals the formula $2CS_2 + H_2O$; Wartha, later still, considered it to be solid carbon bisulphide. Ballo put some carbon bisulphide into a shallow vessel, and directed a current of air on it, so as to strike the surface at an acute angle; with *undried* air, the formation of a snowy solid was particularly observed at the point where the current divides the liquid like a wedge, while a general formation of flakes took place in the rest of the liquid. Air, *dried* by calcium chloride, gave no formation of snow; or at most, a very slight formation. Some of the snowy substance was freed from

* This number is certainly wrong.—C. S.

† Deut. Chem. Ges. Ber., iv, 118.

liquid carbon bisulphide by a current of air, and the amount of water determined by a method of Duclaux's. Three experiments gave 17·3, 36·14, 27·09 as the percentages of water. The possibility of formation of ice from excess of moist air, or of loss of carbon bisulphide during the purification, would well account for the variable numbers.

In order to see whether water is really necessary for the formation of the solid substance, the author directed the air current on the bisulphide covered with a layer of absolute alcohol, so that the air on reaching the bisulphide is thoroughly dried; in this case the snowy substance was not formed. He concludes from this that water is necessary for the production of this body, and regards it as a solidified solution of liquid carbon bisulphide in water, or of water in carbon bisulphide.

F. Sajóhelyi* and M. Ballo have tried the effect of a current of moist air directed on to the surface of chloroform and ethyl iodide. The same formation of snow was observed, as in Ballo's experiments with carbon bisulphide; the chloroform snow was shown to contain water and chloroform by melting in a test-tube. In the case of chloroform the temperature fell to $-13°$, in that of ethyl iodide to $-9°$.

W. H. D.

On Chloride of Iodine. By L. Henry.†

Chlorine gas is passed into water in which iodine is suspended, and solid potassium chlorate is added in the proportion of 122·5 parts for every 127 of iodine originally employed. On warming the liquid chlorine it evolved, $KClO_3 + ICl = KIO_3 + ClCl$; and on cooling, potassium iodate crystallises out. The author recommends this as a convenient method of preparing the latter salt. If some iodine trichloride is formed in the first stage, it will not interfere with the success of the preparation, since it reacts with potassic chlorate in the same way as the monochloride.

C. H. G.

On the Isomorphism of Sodic Nitrate with Calc-spar.‡

It is well known that the crystalline forms of sodic nitrate and calc-spar are almost identical. The two compounds contain also the same number of atoms in the molecule, and their molecular volumes are nearly equal. It is then certain that they will be isomorphous; this can be easily proved by a simple experiment. A crystal of calc-spar is taken, and the surface cleaned by the action of dilute nitric acid; it

* Deut. Chem. Ges. Ber., v, 160.

† Zeitschr. f. Chem. [2], vii, 56; from Deut. Chem. Ges. Ber., iii, 892.

‡ Deut. Chem. Ges. Ber., iv, 104.

is then hung in a warm saturated solution of sodic nitrate, when the crystal will grow with perfect regularity, proving the actual isomorphism of $CaCO_3$ and $NaNO_3$, or perhaps $Ca_2C_2O_6$ and $Na_2N_2O_6$. (Lothar Meyer, *Deut. Chem. Ges. Ber.* iv, 53).

G. Rose observes that this experiment has already been described by Sénarmont in the Comptes rendus for 1854, xxxviii, 105. Mitscherlich repeated the experiment, but instead of using a crystal of calc spar he used one of dolomite (bitter spar). The surface was cleaned with dilute nitric acid, and then placed in a saturated solution of sodic nitrate, when the crystal grew with perfect regularity.

Arragonite and potassic nitrate are isomorphous; a crystal of the former, when placed in a saturated solution of potassic nitrate, will grow and increase regularly. Potassic nitrate can also crystallise in the form of calc-spar, as Frankenheim* has proved, so that calcic carbonate and potassic nitrate are isodimorphous; probably sodic nitrate belongs to this group, but it is not yet proved.

A. P.

Experiments on the Oxidation of Iron. By F. Crace Calvert.†

The author found the composition of two samples of iron rust to be—

	from Conway bridge.	from Llangollen.
Sesquioxide of iron	93·094	92·900
Protoxide of iron	5·810	6·177
Carbonate of iron	0·900	0·617
Silica	0·196	0·121
Ammonia	trace.	trace.
Carbonate of lime	—	0·295

On exposing slips of bright iron to atmospheres of dry or moist oxygen, or of carbonic acid, or of mixed oxygen and ammonia, either dry or wet, or of dry oxygen and carbonic acid, he found no oxidation to take place, but by employing the last-named mixture in a damp state, rust was produced in a few hours.

In accordance with these facts, it was further shown that a natural water, which caused iron to rust rapidly, was deprived of that power by long boiling. The observation of Berzelius, that the alkalies prevent the rusting of iron, was extended so as to show that their carbonates and bicarbonates possess the same power.

C. H. G.

* Pogg. Ann. Bd., 40, s. 455.

† Chem. News, xxiii, 98.

On a Chromium Derivative, obtained by Heating Potassium Dichromate with 2 pts. Concentrated Nitric Acid. By L. DARMSTADTER.*

THE liquid on cooling deposited magnificent crimson tabular crystals, which contain nitric acid. Its aqueous solution yields, not the original salt, but potassium dichromate. When heated, the salt melts to a blackish-brown liquid, at the same time giving off red fumes. The mean percentage of chromium in the crystals was 36·4; from this, the author formulates the compound as $CrO_2\begin{matrix}OK\\NO_2\end{matrix}CrO_3$, which requires 36·7 per cent. Cr. An excess of nitric acid appears to convert this body into $CrO_2\begin{matrix}OK\\NO_2\end{matrix}2CrO_3$.

W. H. D.

On the Basicity of Uranic Oxide, Molybdic Acid, Boric Acid, and Nitrous Acid. By A. C. SCHULTZ-SELLACK.†

URANIC oxide is known to be the only oxide of a multivalent metal that in combination with acids appears to be monobasic. It bears the same relation to the oxides of other trivalent metals that, among acids, nitrous acid bears to phosphorous acid. With its acid compounds, those of molybdic acid, boric acid, and nitrous acid completely correspond:

$(UO)_2SO_4$;	$H(UO)SO_4$:	$(UO)_2SO_4 . SO_3$.
$(MoO)_2SO_4$:	——	——
——	$H(NO)SO_4$:	$(NO)_2SO_4 . SO_3$.
——	——	$2H(BO)SO_4 . SO_3$.

Normal uranic sulphate, $(UO)_2SO_4$, separates, by the evaporation of its solution in concentrated sulphuric acid, in anhydrous, amber-yellow, non-fluorescent crystals. It is not decomposed by a dull red heat. It is largely, but only gradually, soluble in water, and on exposure to the air slowly attracts moisture. *Acid uranic sulphate*, $H(UO)SO_4$, crystallises out on cooling a hot solution of the sulphate in not-fully concentrated sulphuric acid. It is obtained in larger, greenish-yellow, fluorescent crystals by the slow evaporation of the solution at 200° in an open dish. It is very deliquescent. *Anhydro-uranic sulphate*, $(UO)_2SO_4SO_3$, separates after some time in small yellow crystals from a solution of the sulphate in excess of concentrated sulphuric acid mixed with fused sulphuric anhydride. It shows great avidity for moisture, and hisses when water is poured on it.

Molybdic-acid sulphate, $(MoO)_2SO_4$, separates in colourless brilliant

* Deut. Chem. Ges. Ber., iv, 167.

† Deut. Chem. Ges. Ber., iv, 12.

crystals on evaporating a solution of molybdic acid in moderately concentrated sulphuric acid. The crystals are very deliquescent, and are readily decomposed by heat, sulphuric anhydride being given off. Their aqueous solution dries up *in vacuo* to a horny mass. The author has failed to obtain the compound described by Anderson,* $Mo_2(SO_4)_3 + 2H_2O$.

Boric-acid sulphate, $2H(BO)SO_4 . SO_3$, separates after some time in leaf-like crystals on dissolving boric acid in concentrated sulphuric acid and adding sulphuric anhydride, or on dissolving boric acid in fuming sulphuric acid. The crystals fuse when heated and evolve sulphuric anhydride. This compound cannot therefore be regarded as $B_2(SO_4)_3 + H_2O$.

Péligot could not obtain a normal salt of the sexbasic oxide of antimony, and therefore supposed this oxide to have, like uranic oxide, a lower basicity; and Heintz could not obtain the normal sulphate of sexbasic oxide of bismuth. The author finds that the normal sulphates of the sexbasic oxides of antimony and bismuth can easily be obtained anhydrous and crystalline.

Antimony sulphate, $Sb_2(SO_4)_3$, separates in long needles of silky lustre, on evaporating a solution of antimony oxide in moderately concentrated sulphuric acid. The salt is unaltered in dry air, is decomposed by water, and evolves sulphuric anhydride when ignited.

Bismuth sulphate, $Bi_2(SO_4)_3$, is obtained in the same way as the antimony salt, in fine needles, which can be heated nearly to redness without being decomposed.

E. D.

The Titanic Acid Crystallised from Microcosmic Salt is not Anatase. By W. Knop.†

The interesting experiments of G. Rose "On the preparation of crystalline substances by means of the blowpipe,"‡ and especially on the allotropic states of titanic acid, induced the author to repeat them on a larger scale by the aid of a Perrot's gas furnace, whereby he hoped to obtain the crystals of sufficient size for goniometric measurement, or by a determination of the specific gravity and other physical properties, to obviate the uncertainty necessarily attendant on microscopic observation.

Titanic acid crystallises easily from fused borax, partly in the combination ∞P.P., partly in long slender prisms (sagenite) or knee-shaped twin crystals; from microcosmic salt, according to G. Rose, it separates

* Berzelius Jahresbericht, xxii, 161.

† Ann. Chem. Pharm., clvii, 363.

‡ Monatsber. Kgl. Acad. Wiss., Berlin, July, 1867.

in flat plates, which he considers to be anatase. Of these crystals the author prepared 10 grm., the largest being about $\frac{1}{3}$ mm. in length, transparent, and of a deep yellow colour. Although they were not large enough for goniometric measurement, they were examined by polarised light, when each individual crystal, in whatever position it might be, distinctly showed polarisation colours, indicating that they probably belonged to the *rhombic system*, and not to the quadratic.

The specific gravity of the substance, which when examined under the microscope appeared quite homogeneous, was found to be only 2·9, whilst anatase, the lightest modification of titanic acid, has a specific gravity of 3·890 to 3·927. It was necessary, therefore, to determine whether this was a new modification of titanic acid, or a chemical combination. For this purpose it was fused with potassium carbonate, and dissolved in hydrochloric acid, excess of ammonia was added, and the precipitated titanic acid was collected and weighed. The filtrate was found to contain *phosphoric acid*, which was determined in the usual way. The results of the analysis corresponded with the formula $3TiO_2.P_2O_5$. The crystals obtained from the solution of titanic acid in fused microcosmic salt are, therefore, *not anatase* but *phospho-titanic acid*.

Further research will be necessary to ascertain whether the crystals obtained by G. Wunder* under similar circumstances from stannic and zirconic acids are likewise phosphoric acid compounds.

C. E. G.

Formation of Azurite. By F. Wibel and E. Tüngel.†

The authors repeatedly examined considerable quantities of the Siberian mineral for ammonia, with negative results, thereby invalidating the supposition that its intense colour is due to a combination with ammonia, as is the case with some other salts of copper, and that it has been formed from malachite in presence of nitrogenous matter. They found, moreover, on heating fragments of marble to 200° in a sealed tube, with solution of cupric sulphate, that the marble became covered with a green carbonate, which, on standing for some months, was converted in many places into a deep-blue carbonate, whilst at the same time the whole of the water in the tube disappeared, and numerous crystals of gypsum were deposited. The small quantities of the two carbonates formed, and the difficulty of separating them, have hitherto precluded the possibility of analysing the blue compound quantitatively; its external characters, however, agree so perfectly with those of the natural mineral, that it seems highly probable that azurite has been

* Journ. f. prak. Chem. [2], ii, 1870, 206.

† Deut. Chem. Ges. Ber., iv, 138.

formed from malachite by absorption of carbon dioxide and elimination of water, as in this experiment. J. R.

On an Alloy of Lead with Platinum. By A. BAUER.*

AN alloy of three parts pure lead and one part platinum was rubbed to powder and exposed in a moist state to the action of air, carbonic acid, and vapour of acetic acid. White lead was formed, and was removed from the mass from time to time by treatment with dilute acetic acid; the remaining mass being each time returned to the bell-jar till no further action took place. The crystalline steel-grey powder so obtained was mixed with a small quantity of black finely-divided platinum, which was removed by levigation.

Analyses of the steel-grey powder gave—

Platinum.....	49·13	49·10	46·02	48·86
Lead.....	—	—	—	50·97

The formula PtPb requires 48·82 per cent. platinum and 51·18 per cent. lead.

This alloy is not altered by boiling with acetic acid, but is easily decomposed by mineral acids. Its specific gravity = 15·77.

C. H. G.

On Beryllium-Platinum Chloride. By JULIUS THOMSEN.†

To obtain this compound, pure beryllium hydrate (which was freed from ammonia by heating it with bromine water) is dissolved in a solution of platinic chloride. It is very readily soluble in water, and separates from a hot concentrated solution as an orange-coloured crystalline powder. If its solution is slowly evaporated, it crystallises in short four- or six-sided prisms, with angles of 90° and 135°. Crystallised under the microscope, it forms four-, six-, or eight-sided tables, with the same angles, sometimes also octahedrons, apparently belonging to the quadratic system.

Its composition is $PtCl_4.BeCl_2 + 9H_2O$. Neither this formula nor its crystalline form corresponds to the magnesium salts, $PtCl_4.MgCl_2 + 6H_2O$ and $PtCl_4.MgCl_2 + 12H_2O$, but it agrees with that of the calcium salt, which, according to Topsoé, is $PtCl_4.CaCl_2 + 9H_2O$. This salt does not crystallise well, so that its form could not be determined.

* Zeitschr. f. Chem. [2], vii, 55, from Deut. Chem. Ges. Ber., iii, 836.

† Zeitschr. f. Chem. [2], vii, 45.

The beryllium salt loses 5 molecules of water at 120°, and may then be heated up to 200° without any further loss. The dried salt, $PtCl_4$ $BeCl_2 + 4H_2O$, therefore corresponds to the barium salt, which crystallises from its solution with 4 molecules of water, $PtCl_4.BaCl_2 + 4H_2O$.

C. S.

Mineralogical Chemistry.

Gold from Vancouver's Island. By F. WIBEL.*

A PORTION taken from a finely crystallised specimen of the mineral, weighing 26½ grammes, had the sp. gr. 18·5 at 22°, and yielded on analysis 91·86 p. c. gold, 6·63 silver, 1·00 copper, and 0·51 iron. Mercury, lead, and other metals were not found.

J. R.

On the Formula of, and Percentage of Gold in, the Arsenical Pyrites of Reichenstein in Silesia. By C. GÜTTLER.†

The arsenical pyrites of this locality occurs in pockets, and is very rarely acicular. The specific gravity determined from three specimens was 6·97, 7·05, 7·41. The analysis of the compact variety (I and II) and the acicular crystals (III) gave the following results:—

	S.	As.	Fe.	Gangue.
I.	1·93	66·59	28·28	2·06 = 98·86
II.....	1·97	67·81	28·19	1·14 = 99·11
III....	1·02	66·57	31·08	0·92 = 99·59

The compact kind, whose formula is $FeAs_2$, agrees with the crystallised arsenical pyrites of Norway, Styria, Saxony and the Hartz; the crystallised arsenical pyrites of Reichenstein corresponds in point of chemical constitution with the formula Fe_2As_3. It was not possible to ascertain whether the gold present in the above pyrites was in combination or in the free state; it amounted to 0·312 per cent.

W. F.

Analysis of Graphite from Styria. By J. STINGL.‡

THE specimens were from the graphite mines of the Trieben-Rottenmann Mining Company, which extend from Gaishorn to Lorenzen and

* Deut. Chem. Ges. Ber., iv, 139.

† Jahrbuch für Mineralogie, &c., 1871, i, 81.

‡ Dingler's Polyt. Jour., cxlv, 115.

Singsdorf to Einöd, near Rottenmann, in Upper Styria. They exhibit a marked foliated structure, high metallic lustre, and have an average specific gravity = 2·1443. The author found his results accorded perfectly, whether he burnt the graphite direct in an oxygen stream, or treated the material, before the combustion, with hydrochloric acid, hydrofluoric acid, aqua regia, and hot water successively.

In burning the graphite in oxygen, the precaution should be taken of distributing the material, in as finely-divided a powder as possible, in a very thin layer in the platinum-boat. Combustion in air produces pretty good results, but can do so only when iron sulphide is absent. When the sulphide is present, the employment of the oxygen stream, as in elementary analysis, is of advantage in enabling the operator to collect and determine the sulphurous anhydride.

The estimation of carbon and ash in three different samples of crude graphite gave the following numbers :—

	I.	II.	III.
Carbon	85·00	87·16	82·21
Ash	14·89	12·66	17·92
	99·89	99·82	100·13

A complete analysis of another specimen, collected before elutriation and removal of the included quartz, had the following composition :—

Carbon.	Silica.	Alumina.	Ferric oxide.	Mangano-manganic oxide.	Lime.	Alkalies.
82·4	12·38	3·9	0·53	0·62	0·02	trace. = 99·85

The above quartz contained 99·2 per cent. of silica.

Two other specimens were analysed; the one (I) after elutriation with Schön's apparatus, and the other (II) was washed at the mine from an inferior kind of graphite, from the wall of the mine. They gave these results :—

	Carbon.	Silica.	Alumina.	Iron and manganese oxide.	Alkalies.	Sulphur.	Loss by igni-tion.	
I. ..	81·1	11·61	5·6	2·0	traces.	—	—	= 100·31
II...	55·8	21·00	14·56	4·84	0·62	0·3	2·43	= 99·55

W. F.

Plumbocalcite, from Carinthia. By H. Höfer.*

On a yellowish crystalline limestone of Bleiberg are found rhombohedrons, sometimes 4 mm. long, and remarkable for their brilliant silky

* Jahrbuch für Mineralogie, &c., 1871, i, 80.

lustre. These crystals, according to R. Schöffel's analysis, are composed of calcium carbonate 75·85, and lead carbonate 23·75 (= 99·60).

The peculiar lustrous crust of the rhombohedrons has a specific gravity = 2·92. Schöffel found it to be made up of calcium carbonate 85·84, and lead carbonate 14·13 (= 99·97).

The limestone, forming the matrix of the plumbocalcite, has a specific gravity = 2·881 and three specimens have the following composition:—

	I.	II.	III.
Calcium carbonate	94·18	87·86	95·02
Lead carbonate.....	4·83	9·12	2·42
Zinc carbonate.....	0·94	2·76	2·47
	99·95	99·74	99·91

Plumbocalcite, which occurs at Bleiberg, both spathose and crystalline, had previously been found at the High Pirn Mine, Wanlockhead, in Lanarkshire. Lettsom and Greg have described an interesting specimen of calcspar in pseudomorphs (cubo-octahedrons) after galena, enclosing rhombohedrons of plumbocalcite.

W. F.

Lithiophorite, a Manganese Ore containing Lithia. By A. Frenzel.*

Lithiophorite is amorphous, occurs in compact botryoïdal and reniform masses, in flat shell-like forms, and in pseudomorphs after calcspar. Hardness = 3. Specific gravity = 3·14—3·36. It is bluish-black, with a blackish-brown streak. It gives off water when heated in a tube, does not melt before the blowpipe, but colours the flame dark carmine-red. In this mineral, which is nearly allied to the manganese ores that respectively contain copper and cobalt, there is 1·5 per cent. of lithia. It is found, usually on quartz, in the beds of iron ore of the granite district, near Schneeberg, Schwarzenberg, and Johanngeorgenstadt. The felspar of the granite which is much weathered contains a trace of lithia recognisable with the spectroscope. The mica contains none of this metal.

W. F.

The Occurrence of Zircon in the Hypersthenite of the Radau Valley near Harzburg. By G. Rose.†

While labradorite and hypersthene are essential to the composition of this rock, the following minerals, not essential constituents, are likewise

* Jahrbuch für Mineralogie, &c., 1871, i, 77.

† Jahrbuch für Mineralogie, &c., 1871, i, 77.

met with: titanite and magnetite, both finely disseminated; olivine in small granules of a yellowish-green colour; apatite in minute greenish-white to bright green prisms, traversing the labradorite and hypersthenite; biotite, here and there, in brown plates; and quartz granules of rare occurrence. In addition to these minerals, zircon is met with in very small crystals of the combination ∞ P. P. 3P3, of a white to reddish-white colour, and strong adamantine lustre. The zircon, which is embedded for the most part in the labradorite, resembles in every respect that which is found in such abundance in the gold sand of Columbia, and sparsely in the gold sand of the Urals, and renders it highly probable that both these zircons are from a matrix similar to the Hartz rock. W. F.

The Meteorite of Danville, in Alabama. By L. SMITH.*

A NUMBER of stones fell at 5 p.m. on the 27th November, 1868, near Danville, in Alabama. The one examined had the usual black crust, was of a grey colour on a freshly-broken surface, and was somewhat oolitic in its structure. Troilite and nickeliferous iron were easily recognizable, and another mineral was observed which was probably enstatite. The specific gravity of the stone is 3·398. The iron had the following composition:

Fe.	Ni.	Co.	P.	S.
89·513	9·050	0·521	0·019	0·105 = 99·208

The troilite consists of 61·11 iron and 39·56 sulphur (= 100·67).

The stony portion of this meteorite is made up of 60·88 per cent. soluble and 39·12 per cent. insoluble silicate, the latter being thus composed:

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.
50·08	4·11	19·85	20·14	3·90 = 98·08

These numbers denote a mineral of the augite group. The analysis of the soluble portion (in which were found silica 45·90, magnesia 26·52, iron protoxide 23·64, alumina 1·78, and lime 2·31) yielded numbers corresponding with the constitution of an olivine.

W. F.

The Chlorite Family. By A. KENNGOTT.†

THE author had occasion to reconsider the formulæ which he assigned to chlorite and clinochlore, as well as that of kämmererite and kot-

* Jahrbuch für Mineralogie, &c., 1871, i, 82.

† Jahrbuch für Mineralogie, 1871, i, 51.

schubeite, which differ from the former only in containing chromium, in consequence of the examination by Th. Liebe of a coloured mineral contained in diabase, and named diabantachronnyne, which mineral Liebe found it impossible to place among the chlorite minerals. The results of seven analyses of carefully selected specimens were—

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	FeO.	H_2O.
I	30·27	11·16	—	21·22	26·94	10·20
II.....	29·37	12·00	—	21·01	25·63	11·27
III	29·85	9·07	—	17·92	26·60	15·81
IV	31·25	10·03	3·47	19·73	23·52	11·37
V.....	31·69	12·22	—	22·05	21·26	12·47
VI	31·38	11·89	—	22·91	22·72	10·91
VII	31·56	12·08	—	22·44	21·61	11·78

These numbers yield the following ratios:—

	I.	II.	III.	IV.	V.	VI.	VII.
Silica	5·05	4·89	4·97	5·21	5·28	5·23	5·26
Alumina	1·08	1·16	0·88	0·97	1·19	1·15	1·17
Ferric oxide ..	—	—	—	0·22	—	—	—
Magnesia.....	5·30	5·25	4·48	4·93	5·51	5·73	5·61
Ferrous oxide..	3·74	3·56	3·69	3·27	2·95	3·16	3·00
Water	5·67	6·26	8·78	6·32	6·93	6·06	6·54

The formula $RO.2H_2O + 2(RO.SiO_2)$ has been held to represent the chlorites, &c., on the supposition that alumina is capable of replacing the silicate $RO.SiO_2$. If now we resolve the alumina into AlO_2 and AlO, and add these to the SiO_2 and RO respectively, the same being done in IV with the ferric oxide, we have—

	I.	II.	III.	IV.	V.	VI.	VII.
$SiO_2 + AlO_2$ ..	6·13	6·05	5·85	6·40	6·47	6·38	6·43
RO + AlO ..	10·12	9·97	9·05	9·39	9·65	10·04	9·78
$2H_2O$	2·83	3·13	4·39	3·16	3·46	3·03	3·26
Or,							
$SiO_2 + AlO_2$ ..	2·00	2·00	2·00	2·00	2·00	2·00	2·00
RO + AlO ..	3·30	3·30	3·09	2·93	2·98	3·15	3·04
$2H_2O$	0·92	1·03	1·50	0·97	1·07	0·95	1·01

from which it is assumed that the substance called diabantachronnyne is chlorite. The disparity in III of 1·50 instead of $1(2H_2O)$

doubtless arises from an error in analysis, Liebe having found the exact estimation of the water a difficult problem.

W. F.

On the Formation of Cuprite. By C. GREWINGK.*

THE author describes the opening of a tomb of Pagan times at Dimitrow, in the Telsch district of the Kowno Dominion. At a depth of 120 c.m. below the surface, in a bed of loose yellow sand overlying compact red boulder-clay, were found a number of objects, many of them of metal. Sand being a material in which the corrosion of metallic bodies goes on more rapidly than in peat, or marsh, or water, the bronze was covered with a thick crust of malachite. On opening the grave, Grewingk found a lump of red ferruginous sand, with a necklace of wire thread which was covered over with fragments of skull. In some little cavities in the crust of iron rust that covered the wire, small ruby-red crystals of cuprite ($\infty O \infty . O . \infty O$) were seen. The cuprite evidently arises from the reduction by water containing ferrous carbonate of the ammoniacal solution of copper oxide produced by the reaction of the decomposing human remains on the bronze.

W. F.

On the Constitution of the Granites of Scotland as compared with those of Donegal. By S. HAUGHTON.†

IN his latest contribution to the history of British granites, the author has given the results of his examination of a number of specimens from Scotch localities.

Orthoclase.—I. Flesh-coloured orthoclase crystals, encrusted with crystallised albite, from the eruptive granite of Stirling Hill, Peterhead. II. Large reddish crystals, with muscovite, but free from albite, from metamorphic granite, Rubislaw, Aberdeen. III. White translucent crystals from metamorphic granite, Peterculter, Aberdeen. IV. Large grey crystals from metamorphic granite, Callernish, west of Lewis.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	65·40	19·04	trace	0·22	trace	3·63	11·26	0·20	99·75
II.	64·44	18·64	0·80	0·66	trace	2·73	12·15	0·80	100·22
III.	64·48	20·00	—	1·01	trace	1·72	12·81	0·64	100·66
IV.	64·48	20·00	—	0·78	—	2·19	12·10	0·08	99·63

* Jahrbuch für Mineralogie, 1871, i, 76.

† Jahrbuch für Mineralogie, 1871, i, 83.

The granites of central and western Scotland are metamorphic, like those of Donegal and Norway, with which in fact they are geologically identical; eruptive granite is met with only occasionally, as near Peterhead. The second variety of felspar occurring in metamorphic granite by the side of orthoclase is oligoclase, as is seen at Donegal; the second variety of felspar in the eruptive granite, on the other hand, is albite, as in Mourne, Leinster, and Cornwall. In these respects there is a complete accordance between the Scotch and Irish granites.

Oligoclase and Albite.—I. White opaque oligoclase, without striation, resembling cleavelandite, from the granite of Craigie-Buckler, at Aberdeen. II. Greyish-white translucent oligoclase, with distinct striation, reminding one of the oligoclase of Ytterby, from the granite of Rhiconich, Sutherlandshire. III. Translucent albite, encrusting orthoclase, from the granite of Stirling Hill, near Peterhead.

	SiO_2.	Al_2O_3.	MgO.	CaO.	Na_2O.	K_2O.	Total.
I.	62·00	23·20	—	4·71	9·20	0·43	99·54
II.	61·88	24·80	trace	4·93	8·12	0·98	100·71
III.	68·00	20·00	trace	0·35	10·88	0·68	99·91

Mica.—The two species from the Scotch granites correspond likewise with the two micas from the Donegal granites. I. White mica from the Rubislaw quarries at Aberdeen, where it occurs in large plates associated with orthoclase. The most careful observation failed to detect the presence of lithium in it. II. Black mica from Aberdeen; rarely found in large plates, frequently in scales.

	SiO_2.	SiF_4.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	
I. ..	44·40	0·16	37·36	20·4	—	0·24	0·78	0·57	0·93	9·87	1·84	98·19
II. .	36·15	—	16·50	18·49	6·76	1·80	1·11	7·44	0·92	8·77	1·60	99·89

W. F.

The Variegated Sandstone of the Eastern Rim of the Thuringian Basin. By R. LINCKE.*

THESE triassic sand-beds exhibit, more or less, a crystalline structure in their quartz granules. The form is a hexagonal prism, with usually the corresponding six-sided pyramid, the edges of which are frequently rounded. The bubbles which are almost constantly observed on the sur-

* Jahrbuch für Mineralogie, &c., 1871, i, 15.

face of these granules often have a distinct dark margin, whence it is assumed that these cavities are filled with a colourless transparent fluid. The mica occurring with these granules is of two kinds—yellow or greenish, and brown, and is occasionally found in hexagonal plates. The felspar is more or less weathered, or already converted into kaolin. On the nature of the material cementing these constituents together, depends not only the compactness but the colour of the sandstone. If the cement be ferric oxide, the stone is red; if ferric hydrate, yellow; if manganic oxide, dark brown to black; if clay, limestone, or dolomite, greyish or white; and if kaolin, white like chalk. Lime carbonate invariably accompanied these substances in greater or smaller quantities. Those containing much carbonate were:—the white sand of the Ziegenhain Cave, the green sand at Wöllnitz, the red sand above and below the Rasenmühle near Jena, the red sand of Rothenstein, the white sand of Harpersdorf, and the white sand from the Roda Valley. There is but little carbonate in the sand with blackish-brown markings from between Bibra and Eichenberg.

The elutriation of the specimens from the following localities yielded clayey residues:—The kaolin sandstone of Eisenberg, the red sandstone of Rothenstein, the red sandstone from between Kahla and Rudolstadt, the dolomitic sandstone near the saw-mill at Jena, the sandstone of the Ronneburg heights. Remarkable for their ferruginous cement are:—The red sandstone between Kahla and Rudolstadt, the ferriferous sandstone of the same locality, and the red sandstone of Harpersdorf. A cement very rich in lime occurs in the white sandstone found near Wöllnitz, at Harpersdorf, and in the Roda Valley, while that of the following specimens contains much magnesia:—The red sandstone of Rothenstein, the sandy clay near Wöllnitz, the white sands of the Leutra and the Teufelslöcher near Jena, of Harpersdorf, and that of the Roda Valley. Traces of manganese are present in the cement of the sandstones from the upper beds at Kahla, the lower beds at Harpersdorf, and the lower beds of Thieschitz. A cement in which kaolin predominates is to be met with in the Eisenberg sandstone.

Eight specimens of the sandstones, dried at 80°—85° R., were quantitatively analyzed by treatment with hydrochloric acid; those in which an appreciable amount of the kaolin cement was observed (I, V, and VI), were subsequently acted on by sulphuric acid and sodium carbonate successively; and the amounts of silica, alumina, and ferric oxide dissolved by these reagents immediately precede the "insoluble portion" in the following tables:—

I. Sandstone containing kaolin from Eisenberg.—II. White sandstone above the saw-mill, Jena.—III. White sandstone above the Rasenmühle, Jena.—IV. Red sandstone from Wogau.—V. White sand

stone from Harpersdorf.—VI. White sandstone from the Roda Valley, at Lippersdorff.—VII. Clayey sand from between Jena and Wöllnitz.—VIII. Red clayey interstratum in the sandstone of Rothenstein.

	Dissolved by hydrochloric acid.						Dissolved by sulphuric acid and sodium carbonate.			Insoluble.	Loss.	Total.
	$CaCO_3$.	$MgCO_3$.	$FeCO_3$.	Fe_2O_3.	Al_2O_3.	H_2O.	SiO_2.	Fe_2O_3.	Al_2O_3.			
I.	3·55	3·00	2·40	—	5·85	17·80	101·40	trace	63·92	9799·70	2·38	10,000
II. . .	21·72	16·99	—	10·31	47·77	94·00	—	—	—	9798·53	10·68	,,
III. . .	54·70	2·62	—	7·33	21·14	12·00	—	—	—	9883·97	18·24	,,
IV. . .	118·39	6·74	—	15·11	15·11	53·80	—	—	—	9779·19	11·66	,,
V.	182·68	315·17	—	229·92	24·33	67·10	113·70	trace*	87·40*	8924·22	55·48	,,
VI. . .	397·09	327·79	—	23·54	76·14	110·90	123·20	trace	94·20	8649·45	197·69	,,
VII. . .	134·62	95·91	—	53·50	66·42	136·90	—	—	—	9451·31	67·34	,,
VIII. .	82·21	26·42	—	62·87	33·16	62·87	—	—	—	9606·40	126·07	,,

In I, V, and VI are not inconsiderable traces of potash, due, it is believed, to the cement of these sandstones having arisen from the decomposition of an orthoclase felspar.

The detection of phosphoric acid and the occurrence of hexagonal prisms having the appearance of apatite, in the Harpersdorf sandstone, led the author to examine other sandstones for this acid. He determined the fact of its presence in the white sandstone from the Ziegenhain Cave, that from the upper, middle and lower beds at Harpersdorf, the clayey layer of this locality, the sandy clay from above Kahla, and the sandstone of the Ronneburg heights.

W. F.

Examination of a very compact Swedish Peat. By Oscar Jacobsen.†

Bolley's discovery of paraffin in bituminous shales induced the author to examine different kinds of peat, thinking it possible that paraffin might also exist in them. A very compact peat, of brownish-black colour, from Hör, in Schonen, was selected for this purpose. Peat-moss could be observed only in the upper layers of this substance. The lower portion was denser and darker; freed from pieces of wood its sp. gr. was 1·07. The dried substance gave on analysis 51·38 per cent. carbon, 6·49 per cent. hydrogen, 1·68 per cent. nitrogen, and 5·02 per cent. ash. Ether extracted 3·26 per cent. of solid matter from the

* With phosphoric acid.

† Ann. Ch. Pharm., clvii, 240.

peat. This residue contained no paraffin, but resinous oxygenated bodies; it dissolves partially in alcohol or ether. The portion insoluble in these liquids melted at about 70°, and gave on analysis 81·03 per cent. carbon, and 11·98 per cent. hydrogen. The portion soluble in hot alcohol is a colourless resin, which melts at 74°—75°.

The examination of different kinds of peat showed the existence of resinous bodies, but not of paraffin. The author agrees with Mulder in considering the resin to be a true product of peat-formation, and not formed during the life of the plant. In support of this view, he found only 2·5—2·7 per cent. resin in the *upper* layer of the Swedish peat.

W. H. D.

The Mineral Waters of Neuragoczi, near Halle, on the Saale.
By Dr. STEINBRÜCK.*

THESE springs issue from borings in porphyry rocks on the banks of the River Saale, and pass through clayey marl—from which arise salt and ferruginous springs in considerable number and of varying strength—and, lastly, again through porphyry. The composition of the water, according to Siewert, places the Spa between Marienbad (Kreuzspring) and Homburg (Elizabeth spring). 100,000 parts of spring A and B contained—

Temperature. Sp. gravity.	A 14·5° C. —	B 11·25° C. —
Silica	3·16	3·00
Alumina	2·12	1·34
Ferrous carbonate	2·68	4·06
Potassic sulphate	30·06	32·10
Calcic carbonate	21·30	13·68
Calcic sulphate	32·24	35·19
Magnesic carbonate	—	6·70
Magnesic sulphate	14·47	—
Sodic sulphate	50·08	—
Magnesic chloride	—	5·36
Sodic chloride	1010·00	472·05
Organic matter	5·49	2·66
Total constituents	1171·60	576·14
Free carbonic anhydride	25·21 = 12·76 litres	24·70 = 12·44 itres

The gas which issues from the springs in large bubbles consisted of

98·8 p. c. of nitrogen
·9 „ carbonic anhydride
Traces of oxygen

* Arch. Pharm. cxcv, 97.

Steinbrück adds some considerations on the medicinal properties of these waters, and thinks that spring A may be used with advantage in diseases where Marienbad water has been hitherto recommended, and that spring B fully equals the famous Homburg and Kissingen Spaas, especially the renowned Ragoczi Spaa, and is preferable to most other ferruginous springs, on account of the large amount of sodic chloride and carbonic acid which it contains. W. V.

The Composition of Rhine Water, near Köln. By Dr. Vohl.

This paper commences with some remarks on the difference in composition of spring and river water, pointing out the cause of the softening of the former as it flows from its source. Analyses made by Deville and others of water taken from different parts of the river are then given, from which it appears that the water in passing from Strasburg to Arheim loses 31·242 per cent. of its mineral constituents. The author next gives the results of seven complete analyses made by himself of water taken at different times and from various parts of the river above and below Köln.

As indicative of the mode of operating, and of the general composition of the Rhine at Köln at high water, we give the results of three of these, referring for the details of the others to the original paper.

In 10 litres. Results in grammes.

Suspended matter.	Above Köln.	At Köln.	Below Köln.
Total dried at 100° C.	0·4222	0·3154	0·3829
Loss by ignition	0·1254	0·1294	0·1670
Mineral matter	0·2968	0·1860	0·2159
Soluble matter.			
Residue dried at 100° C.	2·5000	2·4500	2·3000
Consistency of:—			
(*a*) Organic matter, containing nitrogen, &c., by ignition	0·5198	0·2929	0·0055
(*b*) Mineral matter	1·9106	2·0895	2·2127
(*c*) Water of crystallisation and loss	0·0696	0·0676	0·0818
	2·5000	2·4500	2·3000

Composition of Soluble matter:—

Chlorine	0·0247	0·0875	0·0868
Sulphuric acid	0·1957	0·1902	0·2300
Lime	0·7494	0·7815	0·8523
Magnesia	0·2054	0·2141	0·2054
Sodium	0·0160	0·0560	0·0560
Potassium	trace	0·0012	0·0003
Ferric oxide	0·0012	0·0014	trace
Alumina	0·0010	0·0010	—
Silica	0·0040	0·0038	0·0041
Phosphoric acid	0·0061	0·0079	0·0088
Nitric acid	trace	trace	trace
Carbonic acid	0·7071	0·7439	0·7690
Water	0·0696	0·0676	0·0818
Organic matter	0·5198	0·2929	0·0055
	2·5000	2·4500	2·3000

The suspended matter or mud was further examined by agitating the water and allowing the solid matter to subside. The portions which separated first, consisted of sand and fragments of various minerals. The lighter part was principally made up of plant-fibres, fragments of animal substances, hair, wool, bran, &c. The mud left to itself underwent fermentation on the third day emitting sulphurretted hydrogen and other foul exhalations, but living organisms could not be detected. It acted as a ferment when added to sugar solution, and ether separated from it a substance resembling stearic acid.

A. T.

Organic Chemistry.

On the Chemical Structure of some Non-saturated Hydrocarbons.

By A. Butlerow.*

Amongst the different hypotheses brought forward to explain the constitution of these bodies, the author prefers that which assumes that two atoms of carbon are linked together by more than one unit of their combining capacity. This theory explains fully all the well known cases of isomerism in the olefine series; thus we know only one ethylene, one propylene, but three butylenes:—

Ethylene $CH_2{=}CH_2$

Propylene $CH_2{=}CH{-}CH_3$

$$CH_2{=}CH{-}CH_2{-}CH_3,\quad CH_3{-}CH{=}CH{-}CH_3,\quad \begin{matrix}CH_3\\ \diagup\\ \diagdown\\ CH_3\end{matrix}\!\!>\!CH{=}CH_2,$$

Butylenes.

* Chem. Centr., 1871, 89.

The author thinks that the correctness of this theory can be proved by experiment, because then there must exist alcohols or compounds of their radicles with the members of the chlorine group, which do not yield olefines by the abstraction of water, hydrochloric acid, &c. Thus a primary amyl alcohol, having the structure $\begin{array}{c} C(CH_3)_3 \\ | \\ CH_2(OH) \end{array}$, cannot yield an amylene, but a hydrocarbon, C_5H_{10}, which contains a group of three atoms of carbon linked together to a closed chain :—

$$\begin{array}{c} CH_3 \\ | \\ CH_3—C—CH_3 \\ | \\ CH_2 \\ | \\ OH. \end{array} \quad - H_2O \quad = \begin{array}{c} CH_3 \\ | \\ H_2C—C—CH_3 \\ \diagdown \quad | \\ CH_2 \end{array}$$

In the same way isobutylene, $\begin{array}{c} C(CH_3)_2, \\ \| \\ CH_2 \end{array}$ a hydrocarbon discovered and described by the author some time ago, would yield by the loss of two atoms of hydrogen, not crotonylene C_4H_6, but an isomeride with a closed group of three carbon-atoms. But Caventou, who discovered crotonylene, obtained it from butylene prepared by the decomposition of amyl alcohol at a high temperature, and the gases formed by this decomposition contain, as the author has previously shown, a large amount of isobutylene. The author therefore found it necessary to repeat Caventou's experiments with pure isobutylene, which is easily obtained by acting on isobutyl iodide (from the fermentation alcohol) with an alcoholic potash solution. The hydrocarbon was first combined with bromine, and the isobutylene dibromide was converted, by means of an alcoholic potash-solution, into monobrom-isobutylene or isocrotyl bromide, C_4H_7Br, a heavy colourless liquid having a pungent smell. This compound is not acted upon by an alcoholic potash-solution at 100°, and is completely decomposed only by heating it with a strong alcoholic solution of sodium ethylate to 130°. No crotonylene was formed, which boils at 18°, but ethyl-isocrotyl ether $\left.\begin{array}{c} C_2H_5 \\ C_4H_7 \end{array}\right\} O$, a mobile liquid boiling at 92°—94°, and having a characteristic but not strong smell. The author's expectations were thus fulfilled; instead of hydrobromic acid being taken out, bromine was replaced by oxethyl, C_2H_5O, and it appears therefore most probable that Caventou worked with a mixture of isomeric butylenes.

To obtain an insight into the chemical structure of isocrotyl, the author endeavoured to obtain its alcohol; but neither potassium acetate nor water acted on it at a high temperature; concentrated

sulphuric acid produced a resinous matter, and some acetone. By oxidizing the bromide as well as the ether with a solution of chromic acid, only acetic acid was formed. From the formation of this acid and of acetone, it appears very probable that the structure of isocrotyl is expressed by the formula—

$$\begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>\!C\!=\!CH, \text{ and not by } \begin{matrix} H_3C \\ H_2C \end{matrix}\!\!>\!C\!-\!CH_2$$

The bromide treated with silver oxide, yielded silver bromide, metallic silver, and a soluble silver salt; the latter has the composition of silver butyrate, or rather isobutyrate, as isobutyric acid, like isocrotyl, contains the radical $C(CH_3)_2$. The formation of this salt is explained by the equation—

$$C_4H_7Br + 2Ag_2O = C_4H_7AgO_2 + AgBr + Ag_2.$$

Isocrotyl bromide, heated with solid caustic potash for some hours to 100°, is completely decomposed, the products consisting of a small quantity of a gas burning with a slightly luminous flame, and the potassium salts of fatty acids, which appear to be a mixture of caproic, isobutyric, and acetic acids.

The author concludes his paper with a description of some experiments which he made for the purpose of obtaining a propylene of definite chemical structure, but all gave negative results.

C. S.

On the Constitution of Diamylene. By W. v. SCHNEIDER.*

THE author divides the olefines in two groups. *Mono-olenes* are those which are derived from compounds having the general formula $C_nH_{2n+1}R$ (R representing a monad radical) by the abstraction of H R. From the researches of Erlenmeyer, Butlerow, and others, it appears that in the members of this group, two carbon-atoms are linked together by two units of combining capacity.

The second group includes those olefines which are formed by polymerisation of members of the first group. Of the constitution of these *polyolenes* nothing is known, and the author therefore undertook an investigation of *diamylene*, in order to obtain evidence respecting this question.

This hydrocarbon was prepared according to Erlenmeyer's directions, by shaking together one volume of pure amylene with two volumes of a mixture consisting of two volumes of concentrated sulphuric acid and one volume of water, in stoppered cylinders which were immersed in ice-cold water. From the product thus obtained, which boiled at

* Ann. Ch. Pharm., clvii, 185.

150°—170°, pure diamylene was isolated by fractional distillation. It boils at 150°—153° under a pressure of 721 mm., and has a specific gravity of 0·8416 at 0°, and 0·8248 at 20.°

A solution of potassic dichromate in dilute sulphuric acid acts slowly on it in the cold, more quickly on heating; the products consisting—besides carbonic and acetic acids—of a neutral and of an acid oil, which were separated by means of caustic soda.

The acid liquid is partially decomposed by distillation, and therefore does not exhibit a constant boiling point, but it volatilises with steam without decomposition.

Amethenic acid, $C_7H_{14}O_2$, as the author calls it, is isomeric with œnanthylic acid, from which it differs, however, by exhibiting only very feeble acid properties, its salts being decomposed even by carbonic acid. The potassium, ammonium, calcium, and magnesium salts are crystalline and readily soluble in water; the sodium, barium, strontium, and copper salts are amorphous gum-like masses, and also very soluble; the mercury, cadmium, zinc, lead and silver salts are white amorphous precipitates.

By subjecting this acid to the further action of chromic acid solution, it was completely oxidized to carbonic and acetic acids; besides these compounds, a small quantity of a crystalline acid was obtained, which was not succinic acid.

When amethenic acid is boiled for several days with concentrated nitric acid, nitrous fumes are evolved, and it is converted into a reddish yellow oil, which appears to be a nitro-product.

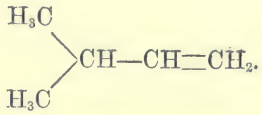
On heating amethenic acid with phosphorus pentachloride, hydrochloric acid is evolved, and a colourless oily chloride is formed—a very unstable body, which soon turns brown, and evolves hydrochloric acid.

The neutral oil which is formed in the oxidation of diamylene, was separated by fractional distillation into fractions boiling between 140°—210°, and a residue which decomposed on further heating. The chief fraction, which boils between 180°—190°, has the composition of *diamylene oxide*, $C_{10}H_{20}O$. It is a light, mobile, colourless liquid, having a penetrating smell, resembling that of camphor. It easily reduces an ammoniacal silver solution, but does not combine with sodium bisulphite. It is the first product of the action of chromic acid upon diamylene, and yields by further oxidation, carbonic, acetic, and amethenic acids.

Phosphorus pentabromide does not act on the neutral oil in the cold; on heating, a quiet reaction sets in, hydrobromic acid and the compound $C_{10}H_{19}Br$ being formed. Probably diamylene dibromide, $C_{10}H_{20}Br_2$, was first formed, a compound which, as Bauer has shown, easily decomposes even at the ordinary temperature. From the results of

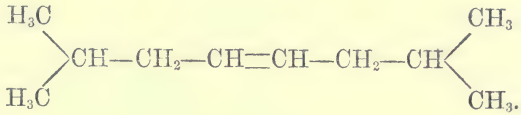
this investigation the author draws the following theoretical conclusions.

Erlenmeyer has shown that amylene has the following constitution:—

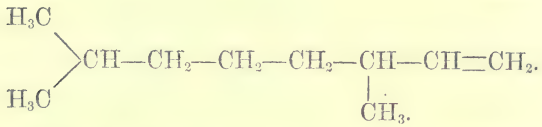


Now as diamylene combines as easily with bromine as amylene does, it might appear most probable that in the former body also, two atoms of carbon are linked together by two units of their combining capacities, and its constitution might be expressed by one of the two following formulæ:—

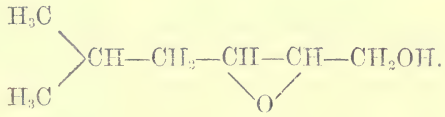
(1)



(2)

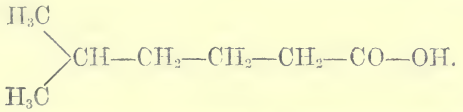


The author, however rejects this view, for the two following reasons:—(1.) If either of the above formulæ expressed the constitution of this hydrocarbon, two atoms of hydrogen would have to change places, and this appears improbable, as diamylene is so very easily formed in the cold. (2.) If the formula (1) is accepted, the constitution of amethenic acid would be



But this would represent an alcohol and not an acid.

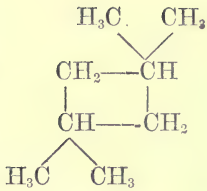
Assuming the second formula, we should have for amethenic acid



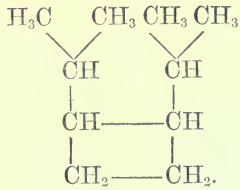
This formula, however, represents a strong acid, as it contains the group carboxyl, CO—OH, and moreover no acetic could be formed at the same time.

The author therefore believes that one of the two following formulæ expresses the true constitution of diamylene:

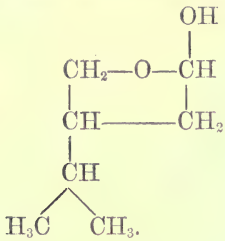
(3)

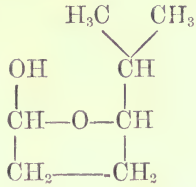


(4)



and the acid would then have one of two formulæ





Both explain why this singular compound is so weak an acid, as both contain the group $\underset{\displaystyle OH}{\underset{|}{HC}}—O$, or carboxyl, $\underset{\displaystyle OH}{\underset{|}{C}}=O$, in which one hydrogen-atom replaces half an oxygen-atom. Whether the constitution of diamylene is expressed by 3 or 4, the author is at present unable to decide.

C. S.

Purification of Benzene. By A. W. Hofmann.*

A sample of light coal-oil which had partially crystallised during the cold of a severe winter, was examined by Dr. Hofmann, in the expectation of obtaining pure benzene from it. The liquid portion was allowed to drain from the crystals, and the latter then distilled. The liquid showed no constant boiling-point; a moderate quantity came over at 80·5° — 81°, more at 82° and 83°, nor had all passed over at 88°. However, by using a Beart's coffee-pot, as recommended by Mansfield, pure benzene was obtained. The cylinder of the piston apparatus used by Dr. Hofmann, was 40—50 cms. high by 8—10 cms. wide.

W. H. D.

The Action of Sulphur on Benzene. By Fr. Schulze.†

Benzene in portions of 1 grm. was sealed up in thin glass tubes; each of these was placed, together with a quantity of sulphur, in the propor-

* Deut. Chem. Ges. Ber., iv, 162.

† Deut. Chem. Ges. Ber., iv, 33.

tion of 64 of the latter to 78 of the former, in a combustion-tube of 100—200 c.c. capacity, which, after exhausting the air, was sealed; thus charged it was placed in an iron tube and heated for two hours in a combustion furnace to a temperature of 400°—500°. Comparatively few tubes exploded, but it was in many cases evident from the appearance of the tubes after heating that the proper temperature had not been observed; either imperfect action of the sulphur had taken place, or the tubes contained carbonaceous bye-products in quantity. From properly heated tubes much hydrogen sulphide escaped on opening; comparatively little unchanged sulphur remained, and but little carbonaceous matter. The contents were extracted with alcohol, the solution evaporated, the residue redissolved in alcohol and allowed to evaporate spontaneously. Long needles were thus obtained, together with yellow crystalline crusts, which exhibit both the smell of diphenyl and the disagreeable properties of sulphur compounds.

H. E. A.

On the Action of Potassium Cyanide on Bromonitrobenzene. By V. von Richter.*

The author has acted upon the bromonitrobenzene obtained from *dinitrobenzene* through *paranitraniline* with potassium cyanide, and finds that, instead of the bromine being replaced, as was to be expected, cyanogen is substituted for the NO_2 group, and a product is obtained, which on heating with potash-solution, yields an acid (probably two are formed) containing bromine, but not the NO_2 group.

The bromonitrobenzene was heated in sealed tubes with alcoholic solution of potassium cyanide for some hours at 180°—200°. Much ammonia escaped on opening the tube, doubtless resulting from the decomposition of the potassium nitrite first formed by the excess of potassium cyanide; in fact a direct experiment, in which potassium nitrite was heated with an alcoholic solution of potassium cyanide, to 200°, showed this to be the case, inasmuch as ammonia was formed in abundance.

Carbonic anhydride and sodium were found to be entirely without action on parabromonitrobenzene dissolved in xylene at a temperature of 140°.

H. E. A.

On Isobutylbenzene and Isobutylanisol. By J. Riess.†

By adding sodium gradually to a mixture of brombenzene and

* Deut. Chem. Ges. Ber., iv, 21.

† Zeitsch. f. Chem. [2], vii, 39.

isobutyl iodide, diluted with a large quantity of ether and surrounded by a mixture of ice and salt, a small quantity of *isobutylbenzene*, $C_6H_5.CH_2.CH(CH_3)_2$, was obtained. It is a colourless liquid, having a strong and pleasant smell; boils at 159°—161°, and has at 16° the sp. gr. 0·8577. Its bromine and nitro derivatives are only liquids, which cannot be distilled without decomposition; the amido compound obtained from mononitro isobutylbenzene forms a hydrochlorate which does not crystallise; neither does it form a crystalline platinum double salt. By oxidising the hydrocarbon with potassium dichromate and sulphuric acid benzoic acid was formed, as was to be expected. The barium salt of the sulpho acid of isobutylbenzene crystallised in fine white scales; readily soluble in water and dilute alcohol, but sparingly in absolute alcohol and ether; the free acid forms transparent rhombohedral needles.

Isobutylanisol, $C_4H_9.O.C_6H_5$, is easily obtained by heating an alcoholic solution of equivalent quantities of phenol, isobutylbromide, and caustic potash.

It is a colourless liquid, which smells like anisol, boils at 198°, and has at 16° the specific gravity 0·9388. The barium salt of its sulpho acid could be obtained only as a white powder, by precipitating its aqueous solution with alcohol. By acting on the anisol with fuming nitric acid carbonization takes place, even if the liquid is kept quite cold.

Para- and *orthonitro-isobutyl-anisol* were obtained by heating the dry potassium salts of the two isomeric nitrophenols with an excess of isobutyl bromide to 180°. The para-compound is a yellow oil having a strong but not unpleasant smell, and boiling at 275°—280°; its specific gravity is 1,1361 at 20°.

The ortho-compound is a dark brown oil, having a very peculiar and pleasant sweetish smell, which, on distillation, boils at 285°—290°, in which operation however, the greatest part is decomposed and a very unpleasant smell is given off. Its specific gravity is 1·1046 at 20°. Neither of these compounds solidifies at −20°, nor are they acted upon by aqueous or alcoholic solutions of caustic potash.

By acting on them in alcoholic solution with tin and hydrochloric acid amido-compounds are formed. The para-compound forms a hydrochloride which crystallised in white ramificated needles, which sublime at 100° in white dendritic-shaped flakes; the platinum double salt crystallises easily in brown-red prisms. The hydrochlorate of the ortho-compound forms an indistinctly crystalline mass, which is completely decomposed on heating; its light yellow platinum salt is very soluble and does not crystallise well. The free amido-bases form white flaky precipitates; they decompose very soon. Both nitro anisols are converted by fuming nitric acid into one and the same dinitro anisol,

a heavy brown odourless oil, which is easily decomposed by an alcoholic potash solution.

C. S.

On the Formation of Aromatic Nitro-compounds in Alcoholic Solution. By BOLLEY.*

ON heating one molecule of phenol with two to three molecules of nitric acid in a flask connected with a reversed condenser, *dinotrophenol* is formed, which crystallises from water in yellow crystals, and melts at 105° (Laurent 104°) Besides this body there is also formed an oil, which appears to be a mixture of mono- and dinitrophenols.

When equal molecules of nitric acid and anthracene are heated in alcoholic solution, the liquid assumes a red colour, and after some time red crystals of *mononitro-anthracene*, $C_{14}H_9NO_2$, separate out (about 80 per cent. of the anthracene). This compound is insoluble in cold alcohol and benzene; from a hot alcoholic solution it crystallises in needles, grouped in stars. On heating it sublimes in needles, which have the greatest resemblance with sublimed alizarine. The formation of this compound in alcoholic solution is the more interesting, as by the direct action of nitric acid on anthracene the pure nitro-compounds are not formed.

If nitro-anthracene is heated with zinc and a solution of caustic potash, the solution colours first red and afterwards yellow. On exhausting it with hot alcohol and mixing this solution with water and hydrochloric acid a body is precipitated, which is soluble in alcohol and benzol, and which on heating sublimes in colourless plates.

Besides the mononitro-compound, there is also *dinitro-anthracene* formed, the quantity of which increases if more nitric acid is employed. It is tolerably soluble in hot alcohol and benzene, and sublimes in colourless plates.

C. S.

On a new class of Alcohols. By C. GRAEBE.†

THE author has prepared the first member of a series which, inasmuch as it contains the $COCH_2(OH)$ complex, may at the same time be looked upon both as alcohol and as aldehyde or ketone. It is a question of considerable theoretical interest whether such compounds would most resemble in properties the alcohols or the acids.

By acting upon boiling *acetylbenzene* (acetophenone) $C_6H_5.COCH_3$ with chlorine, and subsequent fractioning of the product, he obtained *chloromethylbenzene*, $C_6H_5.COCH_2Cl$, as a colourless compound, melting

* Zeitschr. f. Chem. [2], vii, 45.

† Deut. Chem. Ges. Ber., iv, 34.

at 41°, and boiling at 246° : it is insoluble in water, readily soluble in alcohol and ether, and crystallises from dilute alcohol in plates. It has a penetrating smell, and powerfully irritates the eyes. Exposed to light, it rapidly turns green. On oxidation, it yields benzoic acid perfectly free from chlorine, which conclusively proves that the chlorine is contained in the methyl group. It is unchanged by boiling water, but on heating it with water in sealed tubes, hydrochloric acid is formed, and a solid body of very high boiling point.

By the action of an alcoholic solution of potassium acetate, it is converted into the *acetate* of *acetylbenzene-alcohol*, $C_6H_5.COCH_2(OC_2H_3O)$, which melts at 44°, and boils at 270°. On cooling, or by crystallisation from alcohol, it is obtained in large rhombic plates, insoluble in water, readily soluble in alcohol and ether. It has a pleasant aromatic odour.

Acetylbenzene-alcohol, $C_6H_5.COCH_2(OH)$, may be obtained directly from the chloride by heating with a solution of sodium carbonate, or with plumbic hydrate and water, and from the acetate with alcoholic potash-solution: in both cases, however, mixed with considerable quantities of bye-products. In the impure state in which it has hitherto been obtained, it forms a pleasant-smelling body, insoluble in water.

H. E. A.

On some reactions of Stannic Triethide. By A. LADENBURG.*

1. On the addition of a few drops of stannic triethide to an alcoholic solution of mercuric chloride, flocculent mercurous chloride is precipitated, which, on further addition of the stannic compound, is reduced to mercury. Stannic tetrethide does *not* give this reaction.

2. In the cold, ethyl iodide is without action on stannic triethide. Heated in a sealed tube to 220°, the bodies react on one another, and, on opening the tube, a gas escapes, which burns with a faintly luminous flame, the residue consisting of stannic iodotriethide:

$$Sn_2(C_2H_5)_6 + 2C_2H_5I = 2Sn(C_2H_5)_3I + (C_2H_5)_2.$$

3. On gently warming a mixture of stannic triethide with chloracetic acid, lively reaction takes place, and much gas escapes, a mixture of carbonic anhydride and hydrocarbon. On distilling the residue, a body passes over at 220°, which solidifies immediately, and gives with aqueous ammonia, a precipitate insoluble in ether, alcohol, and water, but soluble in warm dilute hydrochloric acid, from which it crystallises in beautiful plates melting at 84·5°. These are pure *stannic diethyl dichloride*. No acid could be detected, and, therefore, the reaction takes place as follows :—

* Deut. Chem. Ges. Ber., iv, 19.

$$Sn_2(C_2H_5)_6 + 2(CH_2Cl.CO_2H) = 2Sn(C_2H_5)_2Cl_2 + 2CO_2 + (CH_3)_2 + (C_2H_5)_2.$$

Stannic tetrethide is similarly acted upon.

4. *Chloracetic ether* is decomposed by stannic triethide only on heating in a sealed tube to 250°. On opening the tube, hydrocarbons escape and the residue contains considerable quantities of stannic triethylchloride. After heating the residue with potash, crystalline stannic triethyl-hydroxide separated out, but no succinic acid could be detected in the filtrate.

Stannic tetrethide decomposes chloracetic ether at a temperature of 300°, when stannic diethyl and triethylchloride are formed.

From these and previous experiments of the author it follows, that the behaviour of stannic triethide is in many instances analogous to that of sodium, and that the two tin-atoms directly united are disunited with peculiar facility by the action of halogens. The converse, viz., the formation of a molecule containing two tin-atoms directly united from molecules containing but one atom of tin, he believes to be highly improbable, although such a reaction has been described by Frankland, who, by the decomposition of stannic diethyl-dimethide, obtained, together with methyl iodide, a liquid of a composition corresponding to the formula $Sn(C_2H_5)_2I$, so that the reaction would be represented by the equation:

$$2Sn(C_2H_5)_2(CH_3)_2 + I_6 = Sn_2(C_2H_5)_4I_2 + 4CH_3I.$$

Against this, however, besides the before-quoted experiments, is the behaviour of stannic tetrethide with iodine, represented by the equations:

$$Sn(C_2H_5)_4 + I_2 = Sn(C_2H_5)_3I + C_2H_5I.$$
$$Sn(C_2H_5)_4 + I_4 = Sn(C_2H_5)_2I_2 + 2C_2H_5I.$$

Stannic tetramethide behaves similarly, and the assumption of the equivalence of ethyl and methyl groups in the tin compounds is therefore legitimate. In that case, in Frankland's experiments, as no ethyl-iodide was formed, first $Sn(C_2H_5)_2CH_3I$, and then $Sn(C_2H_5)_2I_2$ must have resulted. The supposition was therefore not inadmissible that Frankland's product, of the purity of which no guarantee was obtained by distillation or otherwise, was a mixture of *stannic diethyl-methyl-iodide* and *stannic diethyl-iodide*.

The author has therefore repeated Frankland's experiments, but unsuccessfully; the product obtained showed no constant boiling-point, and the quantity prepared did not allow of satisfactory purification. Further experiments are promised.

H. E. A.

* Ann. Ch. Pharm., cxi, 144.

On Stannic Phenyltriethide. By A. LADENBURG.*

A MIXTURE of bromobenzene, stannic iodotriethide and pure dry ether, deposits, on standing for some days, considerable quantities of sodium iodide and bromide; these were removed by filtration, the ether distilled off from the filtrate on the water-bath, and the residue rectified in an atmosphere of hydrogen.

Stannic phenyltriethide, $SnC_6H_5(C_2H_5)_3$, thus obtained is a colourless liquid which distils unchanged at 254°, its vapour being partly oxidised in presence of air. It possesses a slight, not unpleasant odour, is readily soluble in absolute alcohol and ether, difficultly soluble in dilute alcohol, insoluble in water. Its sp. gr. at 0° is 1·2639, and it refracts light somewhat strongly. It burns with a luminous, smoky flame, leaving metallic tin; an alcoholic solution of silver nitrate is immediately reduced by it. Iodine dissolves in it, the colour disappears, and heat is evolved, reaction taking place according to the equation:

$$SnC_6H_5(C_2H_5)_3 + I_2 = Sn(C_2H_5)_3I + C_6H_5I.$$

The products could not be separated by distillation, but readily after treatment with potash, whereby the $Sn(C_2H_5)_3I$ is converted into the crystalline body, $Sn(C_2H_5)_3OH$, of very high boiling point, leaving the phenyl iodide unaltered, which was then distilled off. The latter was characterised by its smell, boiling point, specific gravity, and crystalline nitro-product; the former, by its crystalline form and conversion into the horribly-smelling chloride, $Sn(C_2H_5)_3Cl$, boiling at 205°—208°. Ethyliodide was not formed in this reaction.

Stannic phenyltriethide and stannic chloride react on each other with considerable violence; the former was added drop by drop to the latter, the mixture then heated to boiling and allowed to cool, when the whole solidified. The reaction is expressed by the equation:

$$SnC_6H_5(C_2H_5)_3 + SnCl_4 = Sn(C_2H_5)_2Cl_2 + Sn(C_2H_5)(C_6H_5)Cl_2.$$

Two methods were employed to isolate the products; fractional distillation in an atmosphere of hydrogen, and fractional dissolution with dilute hydrochloric acid. The latter is preferable, although not entirely satisfactory. The *stannic ethyl-phenyl dichloride*, $Sn(C_2H_5)(C_6H_5)Cl_2$, remains as an oil, which slowly solidifies in the cold. Purified by recrystallisation from ether, and dried over sulphuric acid, it melts at 45°, and is converted by ammonia into an oxide, insoluble in ether, alcohol and water, soluble in acids. The author is engaged in the preparation of compounds containing other radicals than phenyl, &c.

H. E. A.

* Deut. Chem. Ges. Ber., iv, 17.

A Lecture-experiment to illustrate the action of dilute Sulphuric Acid on Starch. By A. VOGEL.*

ALMOST all the writing-papers now made contain so much starch that they are immediately coloured dark-blue by weak solution of iodine. When such paper is written upon with dilute sulphuric acid, and, after drying, gently warmed over a flame, care being taken to avoid browning, the starch undergoes alteration. On dipping the paper thus prepared into solution of iodine, it is turned blue, the written characters however remaining white and becoming distinctly legible. As the colour of starch iodide gradually becomes paler and ultimately disappears altogether, the same sheet of paper may be used repeatedly, the blue colour being restored on dipping it into solution of iodine.

J. R.

On the Formation of Pyrocatechin from Cellulose and other Carbohydrates. By F. HOPPE-SEYLER.†

PETTENKOFER failed to obtain pyrocatechin by the dry distillation of straw and paper. The author has heated paper to 210° in a current of carbonic acid, and has also failed to obtain it. The paper very slowly becomes brown, and somewhat more brittle, and yields only a little water and traces of formic acid. But when Swedish filter paper is kept at 200° for 4 or 6 hours along with water in a sealed tube, it turns very brown, and the water becomes yellow and exhibits metallic looking spangles, and films of a brown colour, floating about. On opening the tube a good deal of carbonic acid escapes. The liquid yields by distillation a not inconsiderable quantity of formic acid, and by evaporation over sulphuric acid, a syrup in which pyrocatechin can be easily detected. After mixing it with water, it gives a copious precipitate with lead acetate, but even after complete precipitation, and the separation of the excess of lead by sulphuretted hydrogen, it still yields pyrocatechin when shaken up with ether. The quantity of crystals obtained by the author from the lead precipitate, both by extraction with ether and by sublimation, was too small to analyse, but its identity with pyrocatechin was shown by its behaviour with solvents, caustic soda, ferroso-ferric solutions, lead acetate, silver nitrate, etc.

By the same treatment, starch, cane sugar, and milk sugar, also yield pyrocatechin, but in smaller quantity.

E. D.

* Deut. Chem. Ges. Ber., iv, 140.
† Deut. Chem. Ges. Ber., iv, 15.

New Derivatives of Resorcin. By P. WESELSKY.*

THE action of nitrous acid on resorcin gives rise to a remarkable compound containing nitrogen, in the formation of which 3 mols. of resorcin and 1 mol. N_2O_3 seem to take part. It is a crystalline garnet-red body, which gives a purple-red solution with alcohol, converted into a dark indigo-blue by alkalies.

Both this compound and its products of decomposition are characterised by the beauty and variety of colour which they exhibit.

Pyrogallic acid seems to furnish similar derivatives.

H. E. A.

On Oxypicric or Styphnic Acid. By J. SCHREDER.†

THE author concludes from his researches, that oxypicric acid is identical with trinitroresorcin. Oxypicric acid is reduced by tin and hydrochloric acid, with formation of a crystalline compound, $C_6\left\{\begin{array}{l}H\\OH\\OH\\NH_2.HCl\\NH_2.HCl\\NH_2.HCl\end{array}\right. + SnCl_2$. By treatment with sulphuretted hydrogen, the hydrochloride can be obtained from this compound. Oxidising agents convert the hydrochloride into $C_6\left\{\begin{array}{l}H\\OH\\OH\\NH\\NH\\NH_2.HCl.\end{array}\right.$, a salt crystallising in magnificent blood-red needles, decomposible by ammonia, with formation of the triamine.

Extract of sapan-wood (the best material for the preparation of oxypicric acid), yields resorcin by the action of melted potash. Besides resorcin, a crystalline acid is formed, which is precipitated by lead acetate solution; but its examination is not yet completed.

W. H. D.

A new Process for Converting the Fatty Acids into the Corresponding Alcohols. By ALEXANDER SAYTZEFF.‡

BY the method described in this paper, the author has obtained large quantities of normal butylic alcohol, hitherto only obtained by Schöyen

* Deut. Chem. Ges. Ber., iv, 32. † Deut. Chem. Ges. Ber., iv, 16.
‡ J. pr. Chem. [2], iii, 76.

in such small quantity as to preclude its thorough examination. All the author's attempts to directly convert acetic acid into ethyl alcohol by treating it with different deoxidizing substances, resulted in failure. He therefore turned his attention to acetyl chloride, as the only derivative of acetic acid that can be readily prepared from it in large quantity, and that more easily undergoes chemical changes than the acid itself.

For the conversion of acetyl chloride into ethyl alcohol, a substance had to be chosen which in presence of sodium-amalgam evolved hydrogen without thereby decomposing the acetyl chloride. As such a substance the author employed glacial acetic acid, and by acting on a mixture of this substance and acetyl chloride with solid sodium-amalgam, he obtained ethyl alcohol in considerable quantity.

The conversion of the mixture of acetyl chloride and acetic hydrate proceeds in this way:—The hydrogen generated by the action of the sodium amalgam on the acetic hydrate apparently changes the chloracetyl into aldehyde, which by the further action of hydrogen passes into alcohol; a fresh quantity of acetyl chloride then converts this alcohol into acetic ether, which is the final product of the reaction. Along with this process another reaction occurs, whereby, at the expense of the acetyl chloride and the sodium acetate, acetic anhydride is formed, and this by the nascent hydrogen is also converted into alcohol, which, as in the first case, is obtained as acetic ether. This is shown by treating a mixture of either propionyl chloride or butyryl chloride and acetic hydrate with sodium amalgam, when, besides the particular alcohol, ethyl alcohol is also obtained, which can only be formed from the mixed anhydrides generated by the reaction, since acetic acid cannot be directly changed into ethyl alcohol by deoxidising agents. Hence, in preparing propylic alcohol from propionyl chloride, propionic acid must be employed in place of acetic acid, in order to avoid having to separate the mixed alcohols afterwards; and, for the same reason, in preparing butylic alcohol from butyryl chloride, butyric acid must be used.

Conversion of Acetyl Chloride into Ethyl Alcohol.—Solid sodium amalgam, finely divided, and consisting of 100 parts mercury and 3 parts sodium, was placed in a flask fitted to the lower end of a condenser, and immersed in ice-water. To $1\frac{1}{2}$ molecules of the sodium a mixture of 1 molecule of acetyl chloride and 2 molecules of acetic hydrate was taken, and gradually poured upon the amalgam, keeping the flask constantly agitated, or stirring its contents briskly with a glass rod passing through the cork. After running in all the mixture, the flask was still kept in motion until its contents had become a solid mass, and the whole was then set aside till the next day. Water was then added, and the mixture distilled until oily drops ceased to come over with the water. The distillate consisted of two layers, the upper of which had

a strong odour of acetic ether. This was decomposed by concentrated solution of potash, and an alcoholic fluid distilled off, which, after rectification and drying, proved to be ethyl alcohol; it was further identified by converting it into ethyl iodide. In this way 8 grms. of alcohol were obtained from 60 grms. of acetyl chloride, that is, about 50 per cent. of the theoretical quantity, considering that only half the acetyl chloride is reduced to ethyl alcohol.

Conversion of Propionyl Chloride into Normal Propyl-alcohol.—The propionic acid used boiled between 135° and 143°, and the propionyl chloride between 70° and 80°. They were treated exactly as the acetic acid and acetyl chloride in preparing acetic ether. The final product of the reaction had an agreeable ethereal odour, recalling that of acetic ether, and consisted principally of propyl propionate. To decompose it completely, it had to be sealed up with a concentrated solution of potash, and kept at 130°—140° for 7 or 8 hours. The contents of the tube were then distilled in a retort to dryness. On rectifying the product, one portion came over below 90°, and a second between 90° and 100°. On dissolving some sodium in that which boiled below 90°, and redistilling, one portion boiling below 90° was again obtained, and another boiling above 90°. That boiling below 90° was again treated with sodium, and distilled with the same result, and so on repeatedly. All the portions boiling above 90° were added together, sodium dissolved in them, and the whole distilled, the portion boiling below 90° being separately collected, and that coming over between 94° and 99°. This was again treated with sodium and distilled, when the greater part came over between 95° and 97°. This was perfectly pure propyl alcohol. It is of agreeable alcoholic odour, and boils, under a pressure of 758·31 mm., at 96°; its sp. gr. is 0·823. Mixed and then heated with acid chromate of potassium and sulphuric acid, in a flask provided with a condenser, and afterwards distilled, it yielded an aqueous liquid containing propionic acid (as was ascertained by examining the silver salt obtained from it), and an oily product which dissolved entirely in bisulphite of sodium, though from this solution no crystals could be obtained. This solution, decomposed by potash, again yielded oily drops, which had the smell of aldehyde, reduced silver oxide with formation of a metallic mirror, at the same time forming a silver salt, which proved on analysis to be silver propionate. It may, therefore, be safely concluded that this oily body was propionic aldehyde.

Conversion of Butyryl Chloride into Normal Butyl-alcohol.—The butyric acid employed boiled between 157° and 165°. Butyryl chloride was prepared from this by heating it in a water-bath with phosphorus trichloride, in a flask attached to an inverted condenser, until hydrochloric acid ceased to be evolved. The butyryl chloride was distilled off from the phosphorous acid, and subjected to fractional distillation. In this

way 100 grms. of butyric acid yielded about 100 grms. of perfectly pure butyryl chloride. The treatment of this compound and butyric acid with sodium amalgam was just the same as that of chloracetyl and acetic acid. But the mixture of the butyryl chloride with the butyric acid must be made in the cold, and immediately before it is wanted, as otherwise a reaction sets in, with development of much hydrochloric acid. To avoid the breaking of the flask in comminuting the lumps of amalgam which form during the reaction, an iron apparatus was afterwards employed. The distillate has an agreeable ethereal odour, and consists principally of butyl butyrate. It was decomposed by caustic potash in a sealed tube heated to 150° for 10 hours; the contents of the tube were distilled to dryness; potash was added to the distillate; and the upper oily layer was separated, dried by fused potash, and rectified. The distillate was repeatedly treated with sodium, and fractionated in the same way as in preparing propyl alcohol. Analyses of the product boiling between 115° and 116° gave results agreeing very well with the formula for butyl alcohol. It was oxidized by acid chromate of potassium and sulphuric acid, and an oily body, proved to be butyric aldehyde in the same way as in the case of propyl aldehyde, was obtained, together with an aqueous solution of an acid. This acid was shown to be butyric acid, by preparing and analysing its silver and calcium salts. There could, therefore, be no doubt that the alcohol yielding it was actually the primary, normal butyl alcohol.

Normal butyl alcohol is a colourless liquid, having an odour something like amyl alcohol, but weaker and pleasanter, boiling at 115°—116° under a pressure of 758·31 mm., of sp. gr. 0·826, slightly soluble in water, miscible with alcohol and ether in all proportions, and yielding with sodium a crystalline alcoholate.

Butyl iodide was prepared from this normal butyl alcohol and analysed. It is a heavy liquid boiling at 130°, and having an odour resembling that of ethyl iodide. The iodides isomeric with this have, as is well known, the property of breaking up with tolerable facility into hydriodic acid and butylene when treated with alcoholic potash. The iodide of the normal alcohol gives under these circumstances, and that with difficulty, only a minute quantity of butylene, but, on the other hand, tends to undergo a double decomposition, as will be shown in another paper.

E. D.

On the Compounds of Sodium Acetate with Water. By EMIL ZETTNOW.*

WHEN crystallised sodium acetate is heated, it melts at about 77° to

* Pogg. Ann., cxlii, 306.

78°, and begins to boil at 120°, after some minutes the boiling point rises to 123°; the flask containing the solution is closed with a plug of cotton wool whilst the liquid is boiling; when nearly cold crystallisation takes place with a considerable rise of temperature, the flask is tilted to drain the thick mother liquors from the soft mass of crystals, and allowed to stand for some hours; on removing the cotton-wool plug the mother liquors form a solid crystalline mass. Some of the first formed crystals, which had drained quite free from the mother liquors, were found to have the composition $2C_2H_3NaO_2 + 5H_2O$. These crystals were exposed to a temperature of 125°—126°, when they almost entirely melted; on cooling a crop of crystals was obtained, and when separated from the mother liquors gave numbers agreeing with the formula $C_2H_3NaO_2 + H_2O$. Sodium acetate, when melted and allowed to boil for a few seconds, formed crystals on cooling, which on analysis pointed to the possible existence of a compound of the formula $4C_2H_3NaO_2 + 9H_2O$. Some analyses of crystals obtained from a second melting as described above, agree with the formula $4C_2H_3NaO_2 + 5H_2O$, which may also be a definite compound. A. P.

On the Brominated Derivatives of Acetic Anhydride. By H. Gal.*

All the attempts hitherto made to obtain the bromine and chlorine derivatives directly from the anhydrides of organic acids have been fruitless, bromine and acetic anhydride, for example, merely yielding a mixture of acetyl bromide and monobromacetic acid—

$$C_4H_6O_3 + 2Br = C_2H_3OBr + C_2H_3BrO_2.\dagger$$

The production of these derivatives was of especial interest, as amongst them it was to be hoped that the monobrominated derivative would be found, and thus the equivalent of the anhydride definitely fixed.

The general method given by Gerhardt for the preparation of an anhydride, consists in acting on the potassium or sodium salt of the acid with the chloride of the corresponding acid radical; if now for this chloride we substitute a chloride in which the hydrogen of the acid radical is already replaced by chlorine, an anhydride should be obtained in which one or more atoms of hydrogen are replaced by a corresponding number of chlorine atoms.

Owing to the difficulty of preparing such chlorine derivates of acetyl chloride, the author, in his experiments, employed monobromacetyl bromide (C_2H_2BrO,Br), which, when added to fused and finely powdered sodium acetate, evolved considerable heat: the mixture was

* Compt. Rend., lxxi, 272; Ann. Ch. Pharm., clvii, 369.

† Ann. Ch. Pharm., cxxii, 374, and cxxv, 128.

submitted to distillation. When the liquid thus obtained was rectified, it began to boil at 137°, the temperature gradually rising to 245°, where it remained constant; the product boiling at 245° was analysed, and found to be dibrominated acetic anhydride, $C_4H_4Br_2O_3$. The portion between 137° and 245° was principally acetic anhydride.

It is probable that the reaction takes place in the following manner:—

$$\left.\begin{matrix} C_2H_3O \\ Na \end{matrix}\right\} O + \left.\begin{matrix} C_2H_2BrO \\ Br \end{matrix}\right\} = \left.\begin{matrix} C_2H_3O \\ C_2H_2BrO \end{matrix}\right\} O + NaBr,$$

the action of the monobromacetyl bromide on the sodium salt first producing the monobrominated acetic anhydride, which under the influence of heat, splits up into acetic anhydride and dibrominated acetic anhydride, thus:—

$$2 \left.\begin{matrix} C_2H_3O \\ C_2H_2BrO \end{matrix}\right\} O = \left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O + \left.\begin{matrix} C_2H_2BrO \\ C_2H_2BrO \end{matrix}\right\} O.$$

The new substance does not solidify at 0°. When poured into water it sinks to the bottom, and gradually dissolves, forming monobromacetic acid, which may also be obtained in the crystalline state by exposing the dibrominated anhydride to moist air. The new anhydride dissolves in alcohol, with evolution of heat and formation of ethyl monobromacetate.

C. E. G.

Contributions to the History of Trichloracetic Acid and Trichlorocrotonic Acid. By W. E. Judson.*

Chloral dissolves in fuming nitric acid without any reaction taking place; after standing for 24 hours however it is completely oxidised to trichloracetic acid; if the mixture is heated the oxidation is finished in a few moments. Trichloracetic acid boils at 195°; its lead salt, $Pb(C_2Cl_3O_2)_2 + H_2O$ crystallises in large rhombic prisms; it is readily soluble in water, less so in alcohol, and only sparingly in ether.

The copper salt, $Cu(C_2Cl_3O_2)_2 + 6H_2O$ forms fine crystals, resembling copper sulphate. In preparing it, an excess of copper carbonate must be avoided, or else the acid will be decomposed, chloroform being formed. Trichloracetanilide, $C_6H_5.C_2Cl_3O.HN$, was obtained by gradually mixing etheral solutions of trichloracetyl chloride and aniline; it is insoluble in cold water and only very sparingly in boiling, but easily in alcohol and ether; it crystallises in silvery scales which melt at 82°. *Trichloracetoluidide*, which was prepared by an analogous process from toluidine, crystallises in fine six-sided prisms, which are often an inch long and melt at 102°.

* Zeitsch. f. Chem. [2], vii, 40.

Isobutyl trichloracetate, $C_4H_9O.C_2Cl_3O$, is obtained by heating a mixture of 2 mol. of isobutyl alcohol, 2 mol. of trichloracetic acid, and 1 mol. of sulphuric acid; it is a colourless, heavy liquid, boiling at 187°—189°, and having a pleasant smell.

Trichlorocrotonic acid, $C_4H_3Cl_3O_2$, was prepared by oxidising crotonic chloral with nitric acid. It crystallises in colourless, radiate needles, melting at 44° and boiling at 236°—238°; it is very caustic, destroying the skin. It takes up 33 per cent. of water, and, on the other hand, 25 parts of water dissolve one part of the acid.

By acting upon it with zinc and hydrochloric acid, chlorine is replaced by hydrogen; all the products thus obtained crystallise well: best of all *monochlorocrotonic acid*, which melts at 95°.

Potassium trichlorocrotonate, $C_4H_2KCl_3O_2$, is obtained by adding potassium carbonate slowly and in small quantities to the not too concentrated acid; it crystallises in prisms and is very hygroscopic. *Ammonium trichlorocrotonate*, $C_4H_2(NH_4)Cl_3O_2$, crystallises from alcohol in colourless scales. *Lead trichlorocrotonate*, $(C_4H_2Cl_3O_2)_2Pb + 2H_2O$, was prepared by shaking an ethereal solution of the acid with lead carbonate. On evaporating the solution the salt crystallised in needles arranged in tuft-like groups; it is not soluble in cold water and sparingly in boiling water. *Silver trichlorocrotonate*, $C_4H_2AgCl_3O_2$, was obtained by mixing moist silver oxide with a dilute solution of the acid, and adding silver nitrate and ammonia to the filtrate, until it showed a slight alkaline reaction; the salt was thus obtained as a crystalline precipitate, which was dried in vacuo. The *ethylic ether*, $C_4H_2Cl_3,O_2C_2H_5$, is formed by heating equal molecules of the acid and ethyl alcohol in sealed tubes for some hours to 100°. It is a colourless, heavy liquid, which boils at 212° and possesses an aromatic smell.

Trichlorocrotonyl chloride, $C_2H_2Cl_3OCl$, a heavy liquid, boiling at 162°—166°, was prepared by heating the acid with phosphoric chloride to 120°. Water acts on it only slowly, but by alcohol it is instantaneously decomposed, ethylic trichlorocrotonate being formed.

Trichlorocrotonamide, $C_4H_2Cl_3ONH_2$, is easily formed by pouring aqueous ammonia over the chloride. It is sparingly soluble in cold, more readily in boiling water, and crystallises from alcohol and ether in silvery scales, which melt at 96°.

When silver trichlorocrotonate is heated with water in a flask connected with a reversed condenser, a brisk evolution of carbonic acid takes place, and silver chloride and *dichlorallylene*, $C_3H_2Cl_2$, are formed. The latter is a heavy oil which has a penetrating smell; it boils at 78 and combines readily with bromine. The same compound is obtained by acting on crotonic chloral with caustic baryta—

$$C_4H_3Cl_3O + H_2O = C_3H_2Cl_2 + HCl + CH_2O.$$

or by heating trichlorocrotonic acid with diluted alkalis—

$$C_4H_3Cl_3O_2 = C_3H_2Cl_2 + HCl + CO_2.$$

If the aqueous solution of the acid is acted upon by an excess of silver oxide or alkali, the yield of dichlorallylene is very small, as it is further acted upon.

By heating a mixture of 50 grms. of crotonic chloral with 70 grms. of phosphoric pentachloride for some time to 110°—120° a liquid is formed which boils between 130°—210°, from which, by fractional distillation, *tetrachlorocrotonylene*, $C_4H_2Cl_4$, could be isolated. This compound, which boils at 200°, combines with bromine.

C. S.

On some Derivatives of Propionic Acid. By FAUSTO SESTINI.*

Propionamide, $C_3H_5O.NH_2$, is best prepared by mixing *ethyl propionate* with 5—6 times its volume of strong ammonia, leaving the liquid to stand for 3—4 days, and shaking the mixture from time to time. The liquid is first concentrated on the water-bath, and then evaporated over sulphuric acid to the consistence of a syrup, which is exhausted with ether, the solution evaporated, and the residue recrystallised from ether or chloroform. It is colourless, readily soluble in cold alcohol and ether, from which it crystallises in radiate crystalline masses, or in prisms grouped in fascicles; from chloroform it crystallises in pearly scales. It melts at 75°—76°, and solidifies again at 50°; at a higher temperature it sublimes.

Propionamide hydrochloride, $(C_3H_5ONH_2)_2ClH$, is obtained by passing hydrochloric acid gas into an ethereal solution of the amide; the liquid separates into two layers, the lower of which contains the new compound, which is isolated by washing several times with ether and evaporating over sulphuric acid. It crystallises in needles which are very sparingly soluble in ether; it is deliquescent, readily soluble in water and alcohol, and has an acid reaction.

Mercury-propionamide, $(C_3H_5O.NH)_2Hg$, is obtained in large colourless quadratic plates by heating an aqueous solution of the amide with mercuric oxide to 50°, and leaving the solution to evaporate slowly; it is sparingly soluble in cold, but readily in boiling water.

Propionanilide, $C_3H_5O.NH.C_6H_5$, was obtained by adding drop by drop 3 parts of propionyl chloride to 10 parts of well cooled aniline. It crystallises from water in small micaceous plates, which melt at 92°; at a higher temperature it sublimes partially. By boiling it with acids or alkalis, it is decomposed into propionic acid and aniline.

Neutral ammonium propionate, $C_3H_5O.ONH_4$, forms very fine long prisms. It is very deliquescent, and readily soluble in water and alcohol, but insoluble in ether. If a concentrated solution is allowed

* Cemento iv, 21; Zeitschr. f. Chem. [2] vii, 34.

to stand in a bell-jar over sulphuric acid, an acid salt, $C_3H_5O.ONH_4 + C_3H_6O_2$, crystallises in small quadratic plates. When the neutral salt is distilled ammonia escapes, and between 130°—150° the acid salt comes over, crystallising in hexagonal plates, which melt at 45°.

The best method of preparing propionic ether is, according to the author, to distil a mixture of 24 parts of alcohol (containing 95 per cent.), 18 parts of propionic acid, and 4 parts of sulphuric acid.

C. S.

On β-Iodopropionic Acid. By Wislicenus.*

From the results of former experiments the author came to the conclusion that the acid described by Beilstein as *hydracrylic acid*, $C_{12}H_{22}O_{11}$, does not exist.† He has, therefore, carefully repeated Berlstein's experiments, and finds that the principal product consists of *β-oxypropionic acids*, $C_3H_6O_3$, the sodium salt of which was obtained in a pure state by crystallising it from hot absolute alcohol; this acid, which is not identical with *paralactic acid*, splits up by distillation in water and acrylic acid.

Besides this body, he obtained three other acids, the sodium salts of which are nearly insoluble in alcohol, and the separation of which is very difficult. That which is most soluble in dilute alcohol is *sodium acrylate*, and that which is quite insoluble in alcohol, but very soluble in water, and deliquescent, has the composition $C_6H_8Na_2O_5$; it gives with the solutions of salts of Ca, Ba, Zn, Fe, Cu, Pb, Ag, amorphous precipitates. This bibasic acid is isomeric with *adipimalic* and is probably *paradipimalic acid*.

The third acid, which the author calls *dihydracrylic acid*, is also isomeric with adipimalic acid: its sodium salt is less soluble than sodium acrylate, and not deliquescent; it is not precipitated by calcium and barium salts; with lead salts it gives a precipitate soluble in an excess of the precipitant.

When acrylic, β-oxypropionic, and dihydracrylic acid are heated to 120° with concentrated hydroiodic acid, they are reconverted into β-iodopropionic acid, but paradipimalic acid is not.

These four acids are formed according to the following equations:—

(1) $C_3H_5IO_2 + AgOH = AgI + C_3H_5(OH)O_2$, β-oxypropionic acid.
(2) $C_3H_5IO_2 + AgOH = AgI + H_2O + C_3H_4O_2$, acrylic acid.
(3) $2(C_3H_5IO_2) + 2AgOH = 2AgI + H_2O + (C_3H_5O_2)_2O$, dihydracrylic acid.
(4) $2(C_3H_5IO_2) + 2AgOH = 2AgI + H_2O + C_6H_9(OH)O_4$, paradipimalic acid.

Socoloff, who also has investigated β-oxypropionic acid, regards this

* Zeitschr. f. Chem. [2], vii, 44.

† Beilstein obtained this acid by treating a solution of β-idioproponic acid with moist silver oxide.—C. S.

body as the aldehyde of glyceric acid, because its calcium salt gives a precipitate with calcium bisulphite, but the author has found that this precipitate is nothing but normal calcium sulphite, and is also obtained by mixing solutions of calcium acetate and calcium bisulphite, acetic acid being set free.

Zinc β-oxypropionate forms beautiful crystals $(C_3H_5O_3)_2Zn + 4H_2O$; it is very soluble in water, and melts below 60° in its water of crystallisation; if by stronger heating a part of this water is expelled, the residue does not crystallise on cooling, but remains as a syrup. This is the reason why neither the author in his former experiments, nor Wichelhaus and von Richter succeeded to crystallise this salt; they always evaporated this solution too far down.

When sodium β-oxypropionate is heated water is given off, and a mixture of sodium salts is formed, which dissolves in water, with evolution of much heat. The solution contains the sodium salts of acrylic, dihydracrylic, and paradipimalic acids, which probably have been formed according to the following equations:—

$$(1)\quad C_3H_6O_3 = C_3H_4O_2 + H_2O.$$

$$(2)\quad \begin{cases} (a)\quad C_3H_6O_3 = \underset{\text{Paracrylic acid.}}{C_3H_4O_2} + H_2O. \\ (b)\quad 2(C_3H_4O_2) + H_2O = \underset{\text{Dihydracylic acid.}}{(C_3H_5O_2)_2O}. \end{cases}$$

$$(3)\quad \begin{cases} (a)\quad 2(C_3H_6O_3 = \underset{\text{Analogue of pyrocitric acid ?}}{C_6H_8O_4} + 2H_2O. \\ (b)\quad C_6H_8O_4 + H_2O = \underset{\text{Paradipimalic acid.}}{C_6H_9(OH)O_4}. \end{cases}$$

C. S.

On the History of the Theory of the Constitution of Diglycollic, Diglycollamic, and Triglycollamic Acids. By W. HEINTZ.*

IN the *Journ. für prakt. Chem.* [2] ii, 386, Kolbe has given up his former view of the constitution of these acids, discovered by the author, and adopted another, which he evidently regards as new, but which in reality is exactly the same as that held by the author from the first.

The author's view is that in glycollic acid an atom of aciglycollyl $(C_2H_3O_2)$ and an atom of hydrogen are united by an atom of oxygen, and that in diglycollic acid two atoms of aciglycollyl are bound together by an atom of oxygen. Kolbe, too, holds that in diglycollic acid an

* J. pr. Chem. [2], iii, 69.

atom of oxygen binds together two similar complex atoms, but he calls these "substituted methyl-atoms," and regards them as being each the residue that remains when acetic acid loses an atom of the hydrogen of its methyl. All the views, however, advanced by the author on the subject show that he has always understood by aciglycollyl the residue which remains after the removal from glycollic acid of the hydroxyl attached to that carbon which is in direct combination with hydrogen. For, acetic acid being regarded as aciglycollyl saturated with hydrogen, monochloracetic acid as aciglycollyl saturated with chlorine, and glycollic acid as aciglycollyl saturated with hydroxyl, aciglycollyl may clearly be defined as acetic acid minus one atom of the hydrogen of its methyl.

There is the same absence of any difference between Kolbe's and the author's views respecting di- and tri-glycollamic acids. Passages in the author's papers show plainly that he has held the nitrogen in these acids to be that which binds together the two or the three acetic acid residues.

E. D.

Remarks on the Preceding Communication. By H. KOLBE.*

HEINTZ has endeavoured to show that the author's view of the chemical constitution of diglycollic acid is exactly the same as his own. So far from agreeing with Heintz that in glycollic acid there is an atom of hydrogen united by an atom of oxygen to the univalent radical aciglycollyl (consisting of methylene and carboxyl), the author admits the presence of aciglycollyl neither in glycollic acid nor in acetic and diglycollic acids. Acetic acid contains methyl as a proximate constituent, and not methylene plus hydrogen. So, likewise, is methyl present in monochloracetic acid, glycollic acid, glycocoll, &c.; only in these an atom of hydrogen is replaced by an atom of chlorine, of hydroxyl, and of amidogen respectively. Then, as regards diglycollic acid, although, as Heintz correctly remarks, the author considers that in diglycollic acid an atom of oxygen unites two similar atomic groups, it does not at all follow from this that these groups are aciglycollyl, the presence of which in diglycollic acid, any more than in glycollic acid, the author does not admit. In diglycollic acid an atom of the hydrogen of the methyl of acetic acid is replaced by a half-atom of oxygen, and, as bivalent oxygen is indivisible, this hydrogen is replaced by it in two molecules of acetic acid. In this sense it is that the author regards diglycollic acid as substituted diacetic acid.

The very material difference between the author's view of the constitution of diglycollic acid and the aciglycollyl theory is shown by the

* J. pr. Chem [2], iii, 73.

consideration that, in accordance with the latter, dichloracetic acid must be formed by the addition of two atoms of chlorine to a radical, which evidently cannot be aciglycollyl, and which must be regarded as a new bivalent radical; and that trichloracetic acid must be formed by the addition of three atoms of chlorine to another new radical, which is trivalent.

Lastly, in order to show that the two theories as to the constitution of di- and tri-glycollamic acids are widely different, it will suffice to point out, for comparison with the author's published views, that Heintz admits in these bodies, also, the presence of the radical aciglycollyl in the place of the hydrogen-atoms of ammonia, regarding diglycollamic acid as a secondary organic ammonia, and triglycollamic acid as a tertiary one.

Further observations on this subject have been published by Heintz (*J. pr. Chem.* [2], iii, 120): also by A. Claus (*ibid.* 123).

E. D.

On Amidobenzoic Acid and Carbon Bisulphide. By V. MERZ and W. WEITH.*

ON acting upon amidobenzoic acid with carbon bisulphide in alcoholic solution, sulphuretted hydrogen is evolved, and *dicarboxyl-sulphocarbanilide* $(CO.OHC_6H_4NH)_2CS$ separates in slender white needles, which are nearly insoluble in alcohol, ether, benzol, &c., but readily soluble in alkalies and alkaline carbonates. On heating it with water and barium carbonate, the salt, $C_{15}H_{10}BaN_2SO_4$, is obtained in granular crystals.

The sulphocarbanilide melts only above 300°, with evolution of large quantities of sulphuretted hydrogen; the sulphur in this compound is so loosely combined that it is taken out by several oxides at the common temperature.

C. S.

On Naphthyl-Purpuric Acid. By E. v. SOMMARUGA.†

IN a preliminary note, published some time ago, Hlasiwetz stated, that by acting upon dinitronaphthol with potassium cyanide, a blue body resembling indigo is formed, besides naphthyl-purpuric acid. The author has continued this investigation, and finds that this blue compound is obtained only when the reaction takes place in an aqueous solution, but if dinitronaphthol is acted upon by the cyanide in an alcoholic solution, naphthyl-purpuric acid alone is formed.

The naphthyl-purpurates have a golden-brown colour, with green metallic lustre; the potassium salt, from which the others were prepared, is crystalline. The formula of the free acid, which, however,

* Zeitschr. f. Chem. [2], vii, 45.

† Deut. Chem. Ges. Ber., iv, 94.

cannot be isolated, is $C_{11}H_{17}N_3O_4$; it is formed according to the equation—

$$C_{10}H_6(NO_2)_2O + 2HCN + H_2O = C_{11}H_7N_3O_4 + CO_2 + NH_3.$$

By a similar reaction, Pfaundler and Oppenheim converted dinitrophenol into meta-purpuric acid, which has the composition $C_7H_5N_3O_4$, and not, as those chemists state, $C_8H_6N_4O_4$.

The two other known purpuric acids, viz., phenyl- and cresyl-purpuric acids, are obtained from the trinitro compounds thus:

$$\underset{\text{Trinitrophenol.}}{C_6H_3(NO_2)_3O} + 3HCN + H_2O = \underset{\text{Phenyl-purpuric acid.}}{C_8H_5N_5O_6} + CO_2 + NH_3.$$

$$\underset{\text{Trinitrocresol.}}{C_7H_5(NO_2)_3O} + 3HCN + H_2O = \underset{\text{Cresyl-purpuric acid.}}{C_9H_7N_5O_6} + CO_2 + H_3N.$$

It therefore appears that for each NO_2 one Cy takes part in the reaction, and the author therefore tried to obtain similar compounds from the two isomeric nitro-phenols, but found that potassium cyanide has no action on monitro-compounds.

By oxidising the naphthyl-purpurates with nitric acid, a mixture of mono- and dinitro-naphthol is obtained, and on fusing them with caustic potash, hemimellitic, phthalic, and benzoic acids are formed.

The indigo-blue compound, which the author calls *indophan*, is also a product of decomposition of naphthyl-purpuric acid, and is formed when an alkaline solution of an isopurpurate is boiled for a long time. The best method to obtain it in larger quantities is to boil in a large flask 2 litres of water with 30 grammes of dinitronaphthol and sufficient ammonia to dissolve it, and add a concentrated hot solution of 45 grammes of potassium cyanide. After ten minutes, when the reaction is completed, the contents of the flask are thrown on a filter and washed with boiling water, until it runs through colourless. The insoluble residue, a mixture of indophan and its potassium compound, is decomposed with hot dilute hydrochloric acid, and well washed.

Pure indophan is a violet powder, with green metallic lustre; its potassium and sodium compounds, which are obtained by heating it with a diluted solution of the caustic alkalis, are dark blue powders with a copper-red metallic lustre. Indophan is insoluble in water, alcohol, ether, benzene, and carbon bisulphide. It is soluble in strong sulphuric acid and in hot glacial acetic acid, with a purple colour. It cannot be sublimed; lime and ferrous sulphate do not act on it, but it is easily acted upon by nitric acid and an alcoholic solution of caustic potash; the products thus formed the author has not studied. Fused with caustic potash it yields the same products as naphthyl-purpuric acid. Its composition is $C_{22}H_{10}N_4O_4$, and it is formed according to the equation—

$$2C_{11}H_7N_3O_4 - 2NO - 2H_2O = C_{22}H_{10}N_4O_4.$$

The potassium compound is $C_{22}H_9KN_4O_4$, and the sodium salt $C_{22}H_9NaN_4O_4$.

C. S.

On Cumidic Acid. By P. JANNASCH.*

By oxidising durene, $C_6H_2(CH_3)_4$, with diluted nitric acid, the author obtained—besides the monobasic cumylic acid previously described—an acid which does not volatilise with aqueous vapour. This non-volatile acid he calls *cumidic acid*, $C_{10}H_{10}O_4$; it is homologous with terephthalic, phthalic, isophthalic, uvitic, and xylidic acids.

Cumidic acid is nearly insoluble in cold and in boiling water; scarcely in ether and benzene, but more readily in boiling alcohol. If to this solution benzene is added, the acid crystallises slowly in long transparent prisms. At a very high temperature it sublimes, without previously melting, and condenses in small shining transparent plates.

Calcium cumidate, $CaC_{10}H_8O_4 + 2H_2O$. crystallises in small, very shining, transparent, and very compact prisms. *Barium cumidate*, $BaC_{10}H_8O_4 + 2H_2O$, crystallises in rhombic plates, which have a fine pearly lustre.

C. S.

On Chlorophenolsulphonic Acids. By T. PETERSEN and R. BAEHR-PREDARI.†

IT has been shown by Kekulé, that by the action of concentrated sulphuric acid on phenol, two isomeric sulpho-acids are simultaneously formed; the investigation of the authors proves that, similarly, *mono-chloro-phenol*, C_6H_4ClOH, when acted on by sulphuric acid, gives rise to at least two isomeric *chlorophenol-sulphonic* acids. The chlorophenol was prepared as follows:—3 lbs. of crystallised phenol, mixed with sufficient water to prevent solidification, were subjected to the action of a current of dry chlorine, the mass being carefully cooled to 0° C., as it was found possible, by this means, to prevent the formation of higher chlorinated products in quantity. The flask was tared and weighed from time to time, the operation being stopped when the calculated increase of weight had taken place. The dark red liquid product was washed with water and a little dilute potash, dried over calcium chloride, distilled, again dried over cupric sulphate, as it was found to retain water with great obstinacy, filtered through gun-cotton, and fractioned. Finally, after repeated fractioning, the greater portion was obtained as a liquid boiling constantly between 215°—220°. This, on standing at 0°, solidified almost entirely, and after allowing the still liquid portion to drain away, the pure chlorophenol was obtained in the

* Zeitschr. f. Chem. [2], vii, 33. † Ann. Ch. Pharm., clvii, 121.

form of transparent colourless needles, which melt at 41°, and boil constantly at 218°. It has a pungent, extremely disagreeable odour; is very deliquescent; possesses still higher corrosive properties than phenol; is scarcely soluble in water, but readily in alcohol, benzol, carbon bisulphide, chloroform, and the caustic alkalies.

The body thus obtained is identical with Dubois' chlorophenol,* the product of the action of sulphuryl chloride, SO_2Cl_2, on phenol; he also prepared it by the action of chlorine on phenol.† It is further identical with Schmitt and Cook's‡ chlorophenol obtained by the dry distillation of the platinochloride of orthodiazophenol; and as amidophenol from orthonitrophenol was found by Körner to yield hydroquinone on oxidation, it is no doubt *orthomonochlorophenol.*

By fusion with caustic potash it is converted into hydroquinone, traces of resorcin being formed at the same time, which are probably due to the presence of isomeric bodies in the chlorophenol.

In the preparation of the sulpho-acids the following precautions were observed:—an equivalent quantity of fuming sulphuric acid, sp. gr., 1·90 was added little by little to the chlorophenol, and the whole well shaken, the temperature rose to 75°; after standing 48 hours the product had solidified to a white crystalline mass, which was dissolved in water, and the excess of chlorophenol filtered off. Sufficient barium carbonate was now added to remove the excess of sulphuric acid, and the liquid was then neutralised by potassium carbonate, filtered, and concentrated. After standing 24 hours a potassium salt of the composition $C_6H_4ClSO_4K$ crystallised out in starlike groups of prisms. After further concentration a crop of flat, pointed crystals of the composition $C_6H_4ClSO_4K + 2$ aq. was obtained, and the mother-liquor now contained only small quantities of very easily soluble salts. In a second experiment the mixture of acid and chlorophenol was heated for a day on the water-bath; in this case *no* chlorophenol separated on the addition of water, the second salt, described above, only was obtained; and the mother-liquor contained but very small quantities of easily soluble salts.

When chlorophenol is heated with sulphuric acid to a higher temperature, evolution of gas and carbonisation takes place, and when an excess of acid is employed, the residue contains *di*sulpho-acids.

The above two salts manifestly correspond with those of Kekulé's para- and meta-phenolsulphonic acids; he obtained the meta-acid by acting with sulphuric acid in the cold, and the para-acid by heating to 100°—110°, and also observed the passage of the meta-salt into the para-salt on recrystallisation, from which it is evident that the para-modifi-

* Zeitschrift für Chemie, 1866, 705.

† Ibid., 1867, 205.

‡ Deut. Chem. Ges. Ber., i, 67.

cation is derived from the first formed meta-acid, and that such a reposition of the sulphuric residue takes place, that at the higher temperature it exchanges the meta-position (1 : 3), for the para-position (1 : 4); the latter being the more symmetrical arrangement, explains the greater stability of the para-acid. With monochlorophenol (1 : 2) the reverse is the case, the sulphuric residue most readily taking up the position 3, so that in the metachlorophenolsulphonic acid (1 : 2 : 3) there are three occupied places side by side, over against three unoccupied places; but if the sulphuric residue were to exchange the position 3 for 4 on warming, a body less symmetrical, and therefore less stable, would result. In fact, the product of the action of sulphuric acid on orthochlorophenol in the cold already consists chiefly of meta- and of but little para-acid (1 : 2 : 4); at 100° meta-acid is almost the only product.

α. *Chlorophenolsulphonic acid* (orthomonochlorophenol-metamonosulphonic acid). To prepare the free acid, the excess of sulphuric acid was removed from a solution of the crude product by basic lead acetate, the filtrate saturated with hydrogen sulphide, and then evaporated on the water-bath to the consistency of a syrup; on standing, large tabular, shining, transparent, colourless crystals were formed, of the composition $C_6H_5ClSO_4$ + aq. These are very soluble in water, and deliquesce rapidly; less soluble in alcohol and ether, and still less so in carbon bisulphide; insoluble in benzol and chloroform. They melt at 75°—76°, and are decomposed at 120°. Both the free acid and its salts strike a deep blue-violet colour with ferric chloride, which does not disappear, even after long boiling, in concentrated solutions; acids and alkalies discharge the colour immediately. On fusing the potassium salt with potassium hydrate, *pyrogallic acid*, and some hydroquinone were obtained, and this result, the authors believe, establishes conclusively that in the sulpho-acid three adjacent hydrogens are replaced. On treatment with nitric acid, sp. gr. 1·40, the sulpho acid and its salts all readily yield Dubois' dinitro-chlorophenol, melting point 81°.

Potassium salts.—When crystallised from water, the potassium salt has the composition $C_6H_4ClSO_4K$ + 2 aq., and is obtained in forms of the monoclinic system, which lose the whole of their water of crystallisation at 110°. After repeated recrystallisation from water, it still retains two molecules of H_2O; the metaphenol-sulphate, it will be recollected, was converted into the para-salt by similar treatment. On recrystallising the above salt from strong alcohol, fine, colourless, shining quadratic plates, of the composition $C_6H_4ClSO_4K$ + aq., are obtained, and together with these an anhydrous salt, $C_6H_4ClSO_4K$, in small, transparent, colourless needles. 1 pt. of anhydrous salt is soluble in 2·24 pts. water at 100°, and in 9·25 at 20°. The *sodium* salt, $C_6H_4ClSO_4Na$, is obtained on neutralising a solution of the free acid, &c., in groups of colourless, shining needles. Heated on platinum

foil it swells up, a behaviour especially characteristic of the salts of this acid, and is decomposed. A *lithium* salt, $C_6H_4ClSO_4Li$ + aq., was obtained from the barium salt by double decomposition with lithium carbonate; it is extremely soluble in water. The *ammonium* salt, $C_6H_4ClSO_4NH_4$, prepared from the barium salt and ammonium sulphate, crystallises in long needles, which melt at 230°, but are decomposed at 250°. The *barium* salt, $C_6H_4ClSO_4.Ba.C_6H_4ClSO_4$, prepared from the free acid and barium carbonate, is the least soluble of all the α-chlorophenol sulphates, and crystallises in crusts or granular aggregates of small needles. α-chlorophenol-sulphonic acid, although monobasic, is dihydric, and on adding baryta water to a hot concentrated solution of the above barium salt, a *barium* salt of the composition $C_6H_3ClSO_4Ba$ + 2 aq., separates out in small shining needles, which re-dissolve with difficulty in water. The *calcium* salt, $C_7H_4ClSO_4.Ca.C_6H_4ClSO_4$ + 2 aq., and the *magnesium* salt, $C_6H_4ClSO_4.Mg.C_6H_4ClSO_4$ + 6 aq., were prepared by double decomposition from the barium salt and the respective sulphates. A *basic lead salt* of the composition—

$$3(C_6H_4ClSO_4.Pb.C_6H_4ClSO_4).2PbO + 4\,aq.,$$

was obtained by adding neutral or basic lead acetate to a solution of the potassium salt; after 12 hours standing it separated out in the form of small colourless, hard crystals. *Silver salt.* On the addition of silver nitrate to a concentrated solution of the potassium salt a flocculent precipitate falls down, which rapidly blackens. Crystalline salts of the heavy metals could not be obtained, owing to their great solubility in water.

Ethyl-α-chlorophenolsulphonic acid (α-chlorophenetolsulphonic acid), *Potassium salt*, $C_6H_3Cl(C_2H_5)SO_4K$.—A mixture of 1 eq. potassium salt (dry), 1 eq. potassium hydrate, and 2 eqs. ethyl iodide, was heated in a sealed tube for some hours at 140°. The mixed product was dissolved in alcohol, and allowed to evaporate gradually; first potassium iodide, then undecomposed potassium salt, and finally the new salt separated out; the latter, after recrystallisation from alcohol and water, was obtained in the form of groups of fine, glistening needles, very soluble in water, and melting at 260°.

β-Chlorophenolsulphonic acid (orthomonochloro-paramonosulphonic acid).—The potassium salt, already mentioned in the beginning of the notice, was the only salt of this acid analysed. It forms small prismatic crystals, united in regular, rosette-like groups, which are harder, and somewhat less soluble than the α-potassium salt. It may be recrystallised from water unchanged. With dilute ferric chloride it gives the violet colour. On fusing it with potassium hydrate pyrogallic acid is formed, the para-acid being, no doubt, first converted into the meta-

acid by the high temperature. By the action of nitric acid the same dinitrochlorophenol is formed as from the meta-acid.

Chlorophenol-disulphonic acids.—The barium salt only of a disulphonic acid, prepared by heating chlorophenol with an excess of sulphuric acid for some hours at 100°, was analysed. It was obtained in the form of white crusts, very difficultly soluble in water.

H. E. A.

On the action of concentrated Nitric Acid on the Chlorophenol-sulphonic Acids. By T. PETERSEN and R. BAEHR-PREDARI.*

THE crude solid sulpho-acid, prepared as above, was added in small portions at a time to well cooled nitric acid, sp. gr. 1·40. At first dissolution took place, soon followed however by the separation of a light-yellow, crystalline nitro-compound, containing no sulphur, almost insoluble in cold water. After a time the whole was precipitated by cold water and well washed; on evaporation of the filtrate, first, a small quantity of the same body crystallised out, and finally, oxalic acid.

As the chlorodinitrophenol thus produced was probably a mixture of isomeric compounds, it was converted into potassium salts by neutralisation with potassium carbonate, and the dark blood-red solution concentrated. On cooling, potassium orthochlorodinitrophenate crystallised out in long, slender, crimson needles; on further concentration a brick-red, granular potassium salt was obtained, and lastly, a very soluble vermilion-red salt in fine, short, flat needles. These salts were further purified by repeated recrystallisation, and then decomposed in aqueous solution by dilute nitric acid. The first gave pure *dinitrochlorophenol*—melting at 80°—81°—; the second *monochlorodinitrophenol* melting at 114°—; and the third *dichloronitrophenol* melting at 106°.—The two latter formed together about 10 per cent. of the total yield. A *nitrochlorophenolsulphonic* acid was not obtained in these experiments, but on treating the first dinitrochlorophenol with concentrated sulphuric acid solution took place, accompanied by evolution of NO_2, and later on small granular crystals separated, which are probably such an acid.

Dinitrochlorophenol—melting point, 80·5°—(*α-chlorodinitrophenol*). This body was first obtained by Dubois† from pure orthochlorophenol—melting at 41°, and boiling at 218°—; later, by Faust and Saame‡ from mononitrochlorophenol of melting point 86°—87°, and from volatile nitrophenol; lastly, by Engelhardt and Latchinoff by the replacement of Cl by OH in α-dichlorodinitrobenzene. The authors obtained it

* Ann. Ch. Pharm., clvii, 154.

† Zeitschrift für Chemie, 1867, 205.

‡ Ann. Ch. Pharm., Suppl. Bd., vii, 190.

both from orthochlorophenol, and from α- and β-orthochlorophenol-sulphonic acids by nitration. It is of a light-yellow, almost sulphur-yellow colour; scarcely soluble in cold, more so in hot water, from which it crystallises in fine needles. It is readily soluble in nitric and sulphuric acids, but the greater part is thrown out unaltered on the addition of water. It is easily soluble in alcohol and ether, from which it is obtained in magnificent prismatic crystals, it is also dissolved in large quantity by chloroform. The crystals belong to the monoclinic system; the forms $0P. - P. + P\infty . \infty P . \infty P\infty .$ were observed. Dinitrochlorophenol is volatile in a current of steam. The salts were all obtained by neutralising a solution of the free acid by the respective carbonates.

Potassium salt, $C_6H_2Cl(NO_2)_2OK$.—Long, fine, glistening needles which appear of a beautiful red colour when viewed by transmitted light, and almost white by reflected light; seen in the liquid they have a greenish-yellow metallic lustre. It is very difficultly soluble in cold water, alcohol and ether, more soluble in hot water. *Ammonium salt*, $C_6H_2Cl(NO_2)_2ONH_4$.—Orange to ochre-yellow, fine needles, more soluble in cold water and alcohol than the above salt; it sublimes slowly at 120°. *Sodium salt*, $C_6H_2Cl(NO_2)_2ONa + 3\,aq.$—is obtained in scarlet-red druses, difficultly soluble in cold, more soluble in hot water. From alcohol it crystallises in small red needles. *Barium salt* $C_6H_2Cl(NO_2)_2O.Ba.C_6H_2Cl(NO_2)_2O + aq.$—Fine, glistening, light saffron-yellow needles, very difficultly soluble in hot water. *Lead salt*, $C_6H_2Cl(NO_2)_2O.Pb.C_6H_2Cl(NO_2)_2O + aq.$ Fine, glistening yellow needles, very difficultly soluble in hot water. A lead salt causes a flocculent, almost orange-red precipitate in solutions of the dinitrochlorophenates. The normal *copper-salt* forms saffron-yellow needles, difficultly soluble in water. Silver nitrate produces a carmine-red precipitate in a solution of the potassium or ammonium salt, which recrystallised from hot water, is obtained in fine crimson needles.

Dinitrochlorophenetol, $C_6H_2Cl(NO_2)_2OC_2H_5$, is readily obtained on treating the above silver salt with ethyl iodide, and crystallises from alcohol in long, flat, almost colourless, glistening needles, which melt at 54°—55°, and solidify again at 44; it is almost insoluble in water, easily soluble in alcohol, ether, and chloroform.

Dinitrochlorophenol, $C_6H_2Cl(NO_2)OH$, melting point 114.—This body was obtained on addition of dilute nitric acid to a warm solution of the potassium salt in light yellow scales, difficultly soluble in water, although much less so than its isomeride above described; readily soluble in alcohol and ether. It crystallises from much water in fine, hair-like needles, from alcohol in flat prisms, from chloroform in light-yellow quadratic plates. It melts at 114°, and solidifies at 104°; at higher temperatures it sublimes in delicate, shining scales,

and is also slowly volatilised in a current of steam. Hot nitric acid is without action on it, so that it seems to be derived from some chlorophenol different from orthochlorophenol, probably from *para*-chlorophenol.

Faust and Saame* described a dinitrochlorophenol melting at 111°, which differs, however, both in the properties of the free acid and of its salts from the above.

Potassium salt, $C_6H_2Cl(NO_2)_2OK$ + aq. This salt forms small druses or branched brick-red aggregates much resembling certain lichens, soluble in water. The anhydrous salt has a brilliant carmine-red colour. *Ammonium* salt, $C_6H_2Cl(NO_2)_2ONH_4$ + aq.—Orange-yellow needles, soluble in water, which redden on drying, and volatilise slowly when heated above 120°.

Barium salt, $C_6H_2Cl(NO_2)_2O.Ba.O_6H_2Cl(NO_2)_2O.$ + 2 aq.—This crystallises from hot water in small ochre-yellow needles. *Silver* salt, a red precipitate, obtained in small granular, light-red crystals by re-crystallisation from hot water.

Mononitrodichlorophenol, $C_6H_2Cl_2(NO_2)OH$, melting point 106°.—This body is thrown down on the addition of dilute nitric acid to a solution of its potassium salt as a crystalline, flocculent, light sulphur-yellow precipitate, easily soluble in alcohol, ether, and chloroform very difficultly soluble in water. From much hot water it crystallises in small flat light-yellow needles or scales, similarly from dilute alcohol, from strong alcohol in branched groups of needles. It melts at 106°, and solidifies again at 96°, heated above this it sublimes in fine needles, but detonates when rapidly and strongly heated. It is volatile in a current of steam. Moderately concentrated sulphuric acid dissolves it unchanged, warm, strong nitric acid converts it into dinitrochlorophenol—melting at 80°—81°. It seems to differ from the two dichloronitrophenols of Seifart†—melting point 125°, and of Fischer, Faust, and Saame‡—melting point 122°. *Potassium* salt, $C_6H_2Cl_2NO_2OK$.—Crystallises from water in short, flat, vermillion-red needles, often grouped in druses, which exhibit a greenish-yellow metallic glance by reflected light. This salt is moderately soluble even in cold water. *Ammonium* salt, dark-yellow needles. *Barium* salt, $C_6H_2Cl_2NO_2O.Ba.C_6H_2Cl_2NO_2O$ + aq., forms small orange-yellow columns difficultly soluble in water. *Silver* salt.—The red precipitate produced by silver nitrate, crystallises from much hot water in reddish-yellow glistening needles.

H. E. A.

* Ann. Ch. Pharm., Suppl. Bd., vii, 196.
† Ann. Ch. Pharm., Suppl. Bd., vii, 198.
‡ Ibid., 130, 195.

Dinitrochlorophenol—melting point 69°. By THEODOR PETERSEN.*

THE sulphuric residue in the chlorophenolsulphonic acids is removed, and replaced by the action of nitric acid much less concentrated than that of sp. gr. 1·40. The sulpho-acid was added as before to an acid of sp. gr. 1·33, which was very carefully cooled. It dissolved without evolution of red fumes, a yellow crystalline nitro-product separating after some time, which was further precipitated by the addition of cold water, and well washed. The product was converted into the potassium salt, as before, and the solution evaporated. A difficultly soluble salt, crystallising in flat, glistening, brown-red scales was thus obtained, quite different from the fine dark-red needles of the dinitrochlorophenol—melting at 80°—salt. The author here remarks, that the differences between the various allied nitro-derivatives of phenol are most evident in the potassium salts. In further experiments this salt was obtained mixed with the dark-red needles. It was decomposed by dilute nitric acid, and yielded a dinitrochlorophenol—melting at 69°—which it was only necessary to warm for a short time with concentrated nitric or strong sulphuric acid, to convert it into the isomeride, melting at 80°·5. This new nitro-body is probably identical with that prepared by Engelhardt and Latschinoff,† who obtained from Jungfleisch's two isomeric dinitrodichlorobenzenes by treatment with sodium hydrate, two dinitrochlorophenols, the one melting at 80°, the other at 70°.

From the mother-liquors of the potassium salt, the same brick-red potassium dinitrochlorophenate mentioned in the previous abstract was obtained, and in the same relatively small proportion. From this, and from the fact, that it is unchanged by concentrated nitric acid, the author believes it to be derived from *parachlorophenol*, since on fusing the chlorophenol with potassium hydrate, pyrocatechin was never observed in the product, but together with the hydroquinone, small quantities of resorcin were obtained, as already mentioned. He was also unable to prepare this body from *pure* α-chlorophenolsulphonic acid. Its constitution seems therefore to be most probably 1, 2, 3, 4.

HO . Cl.

This dinitrochlorophenol is scarcely soluble in cold, more so in hot water, from which it crystallises in fine needles. It is readily soluble in alcohol and ether, from which it can be obtained in prismatic crsytals, and still more so in chloroform. It fuses at 69°, and solidifies again at 60°; sublimes slowly on heating, and detonates at higher temperatures.

The *potassium* salt, $C_6H_2Cl(NO_2)_2OK$, crystallises from hot water in long, broad, rhombic plates, of a brownish-garnet-red colour, which

* Ann. Ch. Pharm., clvii, 165.

† Zeitschrift für Chemie, 1870, 234.

exhibit a magnificent golden glance. It is difficultly soluble in water, although less so than the corresponding α-compound. *Sodium* salt, $C_6H_2Cl(NO_2)_2ONa + 7$ aq. A brick-red, voluminous, lichen-like crystallisation, difficultly soluble in water. From alcohol it crystallises in small red needles. *Ammonium salt*, $C_6H_2Cl(NO_2)_2ONH_4$, crystallises from hot water in beautiful, long, flat, glistening ochre-yellow oblique needles or scales, soluble in water. It is volatile, but less so than the corresponding α-salt. *Barium salt.*—Fine, glistening lemon-yellow needles, difficultly soluble in water. *Silver* salt.—The scarlet-red precipitate produced by silver nitrate recrystallised from hot water, is obtained in small scaly crystals of a garnet-red colour.

β-Dinitrchlorophenetol. The above silver salt is readily decomposed on warming with ethyl iodide. This body crystallises from alcohol in long, flat, glistening, almost colourless needles or scales. It fuses at 51°, and solidifies again at 38°. At higher temperatures it sublimes. It is almost insoluble in water, readily soluble in alcohol, ether, and chloroform.

H. E. A.

On the Constitution of the Nitrochlorophenols. By THEODOR PETERSEN.*

THE author first discusses the constitution of volatile nitrophenol, which he considers to be a *meta*-compound, and for the following reasons:—

1. The two known nitrophenols yield one and the same dinitrophenol, as was shown by Körner; this harmonises well with the assumption that in volatile nitrophenol the groups occupy the 1 : 3 position; were they in the 1 : 4 position the formation of two different dinitrophenols might be expected. The same dinitrophenol is also obtained from picramic acid, in which the amido-group in all probability occupies the position 4, since by the partial reduction of dinitrophenol the outer nitro-group is converted into the amido-group (Körner). Clemm's† experiments are also in favour of this view: he found that both from ordinary dinitrophenol by the replacement of OH by Cl, and from chlorobenzene by nitration, the same chlorodinitrobenzene results.

2. Again, the nitrophenolsulphonic acids prepared by Kekulé from volatile nitrophenol, and by Kolbe and Gauhe by nitration of paraphenolsulphonic acid, are identical, and have probably the constitution 1 : 3 : 4. Kolbe and Gauhe expressly state that only the acid prepared by heating for some time to 100°, viz., Kelkulé's para-acid, 1 : 4, yields

* Ann. Ch. Pharm., clvii, 171.

† Deut. Chem. Ges. Ber., iii, 126.

the nitro-product, the acid prepared at ordinary temperatures, viz., the meta-acid, 1 : 3, giving little or no nitrophenolsulphonic acid. This is remarkable when nitrophenol is assumed to be 1 : 4, but quite natural if it is 1 : 3.

3. A body in a certain degree related to volatile nitrophenol, viz., ordinary nitrobenzoic acid, is a meta-derivative, since it may be readily converted into oxybenzoic acid which V. Meyer* has proved conclusively to be a meta-compound.

At present eleven phenols are known containing chlorine and the nitro-group simultaneously.

MONOCHLOROMONONITROPHENOLS.—α. *Orthochloronitrophenol* (1 : 2 : 3), was prepared by Faust and Saame,† both by nitration of orthochlorophenol and by the action of chlorine on volatile nitrophenol. It melts at 86°, and is converted into Dubois' dinitrochlorophenol by the further action of nitric acid.

MONOCHLORODINITROPHENOLS.—Five have been prepared.

1. α. *Orthochlorodinitrophenol* (1 : 2 : 3 : 4), melting point 80°·5; by Dubois from orthochlorophenol; by Faust and Saame by the action of chlorine on volatile nitrophenol and nitration of the product; by Engelhardt and Latschinoff from α-dinitrodichlorobenzene by replacement of Cl by OH; finally, as in the preceding, from orthochlorophenol-sulphonic acid.

Dichlorobenzene, melting at 53°, from which Jungfleisch obtained his two dinitrochlorobenzenes, and Engelhardt and Latschinoff the corresponding dinitrochlorphenols, must be an orthocompound, as α-dinitrochlorophenol was obtained from it. According to Meyer,‡ solid dibromobenzene melting at 89°, is a para-compound, the dimethylbenzene prepared from it by Fittig's method being converted into terephthalic acid on oxidation. Mayer§ states that the same dibromobenzene is obtained from monobromophenol and phosphorus pentabromide, which proves that monobromophenol is also a 1 : 4 derivative. It is to be noted, moreover, that the properties of monobromophenol are very different from those of orthomonochlorophenol; the former is an easily decomposed body, still liquid at − 18°, the latter a perfectly constant crystalline compound melting at 41°. Körner obtained oxybenzoic acid, a representant of the meta-series, by acting on monobromophenol with sodium and carbonic anhydride, a proof that ordinary monobromophenol contains considerable quantities of metabromophenol. By the action of iodine, also, according to Körner, both ortho- and meta-iodophenol are formed, and even under certain conditions para-iodophenol (Hlasiwetz

* Deut. Chem. Ges. Ber., iii, 114.
† Ann. Ch. Pharm., Suppl. Bd., vii, 191.
‡ Deut. Chem. Ges. Ber., iii, 753.
§ Ann. Ch. Pharm., cxxxvii, 221.

and Weselsky)*. From all this it is evident that by the direct introduction of Cl, Br, I, NO_2 and SO_3 into phenol, the reaction is in every case different; it seems that regularly two isomerides are simultaneously formed, the yield of the one or the other varying with the conditions of experiment. If ordinary dichlorobenzene be a 1 : 2, and ordinary dibromobenzene a 1 : 4 derivative, it would seem that two chlorine atoms attract each other more powerfully than two bromine atoms.

2. *β-Orthochlordinitrophenol* (1 : 2 : 4 : 5), melting point 69°; obtained by Engelhardt and Latschinoff from β-dichlorodinitrobenzene, and by the author from chlorophenolsulphonic acid by nitration. It is converted by solution in nitric or even sulphuric acid into its isomeride melting at 80·5°. The author holds that in its formation, in the first instance, the two nitro-groups occupied a position adjacent to the HSO_3 group, and that then SO_3 splits off; its constitution would therefore be 1 : 2 : 4 : 5. Engelhardt and Latschinoff's β-dichlorodinitrobenzene is then also a 1 : 2 : 4 : 5 derivative, which is a perfectly symmetrical arrangement of the groups, each of the two adjacent Cl-atoms being separated from the two adjacent nitrogroups by hydrogen. α-dichlorodinitrobenzene he regards as a 1 : 2 : 3 : 4 compound; in this case, on replacement of Cl by HO, the Cl (1) more distant from the NO_2 group is affected.

3. *α-Parachlorodinitrophenol* (1 : 2 : 3 : 4), melting point 114°. This was obtained from the brick-red potassium salt before described. It was always formed in relatively the same, although not large quantity, by the action of nitric acid on chlorophenol-sulphonic acid, and, as before mentioned, the chlorophenol employed in the preparation of the latter gave, when fused with potassium hydrate, traces of resorcin, together with much hydroquinone. Further, it is unchanged by warming with nitric acid; by violent action, oxalic acid is formed, and picric acid was once observed. All this strengthens the assumption that it is derived from parachlorophenol.

4. *γ-Orthochlorodinitrophenol* (1 : 2 : 5 : 6), melting point 111°. Faust and Saame prepared this modification by further nitration of a residue remaining after distilling volatile chloronitrophenol in a current of steam. It crystallises from water in yellow scales, from chloroform in irregular, six-sided plates. Seifart obtained the same from orthonitrophenol (containing dinitrophenol) by the action of chlorine and then of nitric acid. The author is of opinion that in this nitro-body, on the one side Cl, on the other $2NO_2$ are immediately adjacent to the HO group, and that it has therefore the 1 : 2 : 5 : 6 constitution. This seems to him the more probable, as neither Faust and Saame nor Seifart observed the

* Deut. Chem. Ges. Ber., ii, 523.

formation of picric acid, although they employed red fuming nitric acid.

5. *α-Metachlorodinitrophenol* (1 : 2 : 3 : 4), melting point 103°. This body was first obtained by Griess, by powerful nitration of chlorinated phenol, containing, no doubt, di- or even tri-chlorophenol. Stenhouse obtained the same from picric acid and chloride of iodine. This differs from all the preceding, and picric acid being a 1 : 2 : 3 : 4 derivative, it only remains to assume Cl as occupying the position 3, and the nitro-groups 2 and 4.

Dichloromonitrophenols.—By the action even of concentrated nitric acid on phenol, *tri*nitro-derivatives only are formed, two H-atoms always remain unattacked. If two H-atoms in phenol are already replaced by Cl, mononitro-derivatives only can be obtained; by more powerful nitration, according to the observations of Petersen and others, one of the two Cl-atoms is replaced without very great difficulty by NO_2 and dinitrochloro-derivatives are generated. Petersen believes the Cl-atom adjacent to the HO group to be the one most difficult to replace by NO_2. Picric acid is obtained with difficulty from the dinitrochlorophenols; if the action be too powerful, oxalic acid is produced. He has observed the formation of picric acid from dinitrochlorophenol melting at 114°, in which he supposes Cl to be in the position 4. Three dichloronitrophenols have hitherto been prepared.

1. *α-Orthodichloronitrophenol* (1 : 2 : 3 : 4), melting point 125°, is readily prepared, according to Seifart.* by the action of chlorine on orthonitrophenol. He also states that after reduction, conversion into the diazo-compound, &c., it yields dichlorophenol melting at 65° and boiling at 218°—220°, which Petersen holds to be a 1 : 3 : 4 compound.

2. *α-Metanitrodichlorophenol* (1 : 2 : 3 : 4); melting point, 121°—122°. Fischer obtained this compound by nitration of dichlorophenol (melting point, 43°, B. P. 210). Faust and Saame, by the action of chlorine on volatile nitrophenol; also from chloronitrophenol and chlorine. Schmitt and Glutz by the action of chlorine on nitrophenol-sulphonic acid. Volatile nitrophenol being 1 : 3, all these modes of formation speak for the 1 : 2 : 3 : 4 constitution of this body. Dichlorophenol (melting point 43°) would then be a 1 : 2 : 4 compound.

3. *α-Paranitrodichlorophenol* (1 : 2 : 3 : 4); melting point, 106°. This was obtained in small quantity by nitration of the mixed chlorophenol-sulphonic acids, and is evidently derived from a dichlorophenol originally present in the chlorophenol. By the action of concentrated nitric acid, it is converted into *α-dinitrochlorophenol*. The author considers the not yet isolated dichlorophenol to be a 1 : 2 : 3 derivative.

Trichloromononitro- and *trichlorodinitro-phenols*.—Faust obtained from

* Ann. Ch. Pharm., Suppl. Bd., vii. 198.

the ethyl ether of trichlorophenol (melting point, 67°—68°, probably 1 : 2 : 3 : 4) by the action of a mixture of fuming nitric and sulphuric acids in the cold, a body which he held to be *trichloronitrophenetol*, but did not analyse; by gently heating the acid mixture, *trichlorodinitrophenetol* is said to have been formed.

The following is a tabular arrangement of all the above nitrophenols:—

	Melting point.						
α-Orthochloro-mononitrophenol	86·5°	C_6HO	Cl	NO_2	H	H	H
α-Orthochloro-dinitrophenol	80·5°	C_6HO	Cl	NO_2	NO_2	H	H
β-Orthochloro-dinitrophenol	69–70°	C_6HO	Cl	H	NO_2	NO_2	H
γ-Orthochloro-dinitrophenol	111°	C_6HO	Cl	H	H	NO_2	NO_2
α-Metachloro-dinitrophenol	103°	C_6HO	NO_2	Cl	NO_2	H	H
α-Parachloro-dinitrophenol	114°	C_6HO	NO_2	NO_2	Cl	H	H
α-Orthonitro-dichlorophenol	125°	C_6HO	NO_2	Cl	Cl	H	H
α-Metanitro-dichlorophenol	121·5°	C_6HO	Cl	NO_2	Cl	H	H
α-Paranitro-dichlorophenol	106°	C_6HO	Cl	Cl	NO_2	H	H
α-Trichloro-mononitrophenol		C_6HO	Cl	Cl	Cl (?)	NO_2	H
α-Trichloro-dinitrophenol		C_6HO	Cl	Cl	Cl	NO_2	NO_2

As already stated, dichlorophenol melting at 43° belongs to the 1 : 2 : 4 series. Dibromophenol melting at 40° appears also to be a 1 : 2 : 4 derivative. Körner obtained from it by nitration, dibromonitrophenol (α-metanitrodibromphenol, 1 : 2 : 3 : 4) melting at 117°—118°; the same is obtained, according to Brunck, by the action of bromine on volatile nitrophenol. This manifestly corresponds to dichloronitrophenol melting at 121°—122°. Again, dinitrobromophenol melting at 78°, prepared from volatile nitrophenol by the action of Br and HNO_3, is evidently the counterpart of α-orthochlorodinitrophenol melting at 80°—5°. Since it is also obtained from crude bromophenol by nitration, this latter might be looked upon as a 1 : 2 derivative, which assumption, however, does not explain certain other reactions, unless it is assumed to be a mixture of the three possible isomerides. According to Laurent, the action of bromine on dinitrophenol yields dinitrobromophenol (parabromodinitrophenol, 1 : 2 : 3 : 4), melting at 110°, corresponding to the above described α-parachlorodinitrophenol melting at 114°. Cl and Br may be replaced in either by NO_2, and so picric acid formed without any great difficulty.

It will be observed that, in all these cases, the melting point of the chlorinated derivatives is from 3° to 4° higher than that of the corresponding brominated compounds; this relation may in future be of very great service in determining the true position of a compound in the series. The following tabular arrangement will render this more evident:—

	Mt. P.		Mt. P.	(1)	(2)	(3)	(4)
Dichlorophenol....	43°	Dibromophenol.....	40°	HO	Cl (Br)		NO_2 (Br)
Chlorodinitrophenol	80·5°	Bromodinitrophenol....	78°	HO	Cl (Br)	NO_2	Cl
Dinitrochlorophenol	114°	Dinitrobromophenol ..	110°	HO	NO_2	NO_2	Cl (Br)
Chloronitrophenol	121·15°	Bromonitrobromophenol	117·5°	HO	Cl (Br)	NO_2	Cl (Br)

H. E. A.

Contributions to the History of the Amido-sulpho-tolulenic Acids. By H. L. Buff.*

By acting upon toluidine with fuming sulphuric acid, two isomeric sulpho-acids are formed. One, which crystallises in needles, and is readily soluble in water and alcohol, has the formula $C_6H_3.CH_3.NH_2SO_3H + \frac{1}{2}H_2O$. It is not decomposed by boiling with a solution of caustic potash, but on distilling it with solid caustic potash, toluidine is reproduced.

The second acid, which crystallises in pale yellow rhombohedrons, is much less soluble in water, and nearly insoluble in alcohol. It is not attacked by aqueous potash, and yields on distillation with solid potash, an oily base, the composition of which could not be determined, as not one of its salts could be obtained in a state fit for analysis.

C. S.

On the Action of Chlorine upon Aldehyde. By G. Kraemer.†

Wurtz has stated that by the action of chlorine upon a solution of aldehyde in carbon chloride he obtained *acetyl chloride* and the compound $C_4H_7ClO_2$. The author on repeating this experiment could not detect the above compounds in the products of the reaction, but obtained the same results again which he had formerly got in conjunction with Pinner.‡

C. S.

Chloral Hydrate and Chloral Alcoholate. By F. Versmann.§

The different crystalline forms in which chloral hydrate is met with, appear to be due to the different solvents used in its purification.

* Zeitschr. f. Chem. [2], vii, 43.

† Zeitsch. f. Chem. [2], vii, 42.

‡ Kraemer and Pinner found that the chief product of this reaction consists of crotonic chloral, $C_4H_3Cl_3O$ (vide preceding paper, p. 234).—C. S.

§ Pharm. J. Trans. [3], i, 701.

Thus water, ether, acetone, benzol, and carbon bisulphide, can be made to give different results. 100 parts of water dissolve 360 parts of the dry hydrate. The alcoholate is also soluble in water, but less so than the hydrate. There is a considerable difference between the sp. gr. of the two substances in the liquid state, viz., sp. gr. of hydrate at 49° = 1·610; of the alcoholate = 1·143 at 40°. A difference is also observable in the sp. gr. of solutions of these substances. Decomposition taking place at the boiling point, its observation affords no criterion of purity.

As, in the ammonia test, some chloroform is dissolved by the water, and some water taken up by the chloroform, this method, though it may serve to decide whether a sample be hydrate or alcoholate, cannot claim analytical accuracy. Dr. Versmann prefers to proceed as follows: 5 to 6 c.c. concentrated sulphuric acid are put into a graduated, well-stopped tube, and heated by placing the tube in water at 60°; 10 grms. chloral hydrate are then added, the whole well shaken, and the tube put back into the hot water. The decomposition is instantaneous, and the anhydrous chloral floating on the acid may be read off as soon as the liquid has cooled down. By about 12 hours' standing, metachloral is produced. In comparative experiments, a somewhat higher result was always given by sulphuric acid than by ammonia.

W. H. D.

The Tests for Chloral Hydrate. By C. H. Wood.*

The author recommends boiling the chloral hydrate in aqueous solution with lime (which he finds to have no sensible action on chloroform), distilling off the chloroform produced, and by measuring its volume, to arrive at the percentage of chloroform. The aqueous portion of the distillate may be tested for alcohol by the iodoform test. He considers the determination of the boiling point to be in some respects a better and simpler test for ordinary use than determining the chloroform.

W. H. D.

Analysis of Chloral Hydrate. By K. Müller.†

Three samples of chloral hydrate manufactured by E. Saame, of Louisenhall were analysed by decomposing with cold solution of potash, with the following results:—

* Pharm. J. Trans. [3], i, 703.
† Chem. News, xxiii, 113.

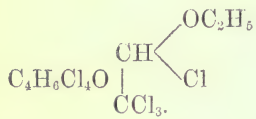
Description.	Boiling point.	Percentage of chloroform.
1. Crystalline cake of dazzling whiteness; agreeable, slightly pungent odour; melting-point, 52°	96·5°	71·9
2. White powder; results same as above..	96·5°	71·9
3. Colourless, transparent, large rhomboïd crystals, with an agreeable odour....	97·3°	71·4

W. H. D.

On the Action of Phosphorus Pentachloride on Chloral Alcoholate.
By L. Henry.*

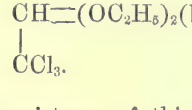
On gently heating a mixture of equal molecules of these two compounds, a brisk reaction sets in, torrents of hydrochloric acid are evolved, and the pentachloride disappears. To the product water was added, to decompose the phosphorus oxychloride. A heavy colourless oil separated out, which has the composition $C_4H_6Cl_4O$; it boils without decomposition at 188°, is insoluble in water, has a pungent smell resembling that of camphor, and a sweetish bitter taste. By a boiling solution of caustic potash, it is decomposed like chloral, chloroform being produced.

The constitution of this compound, which the author calls *chloroxyethyl-trichlorethylidene*, is expressed by the formula—



It is a compound, standing intermediate between

Trichloracetal — Trichlorethylidene dichloride.



$CH{=}(OC_2H_5)_2$(b. p. 230°) and $CHCl_2$(b. p. 158°)

CCl_3. CCl_3.

The existence of this compound throws light upon the constitution of chloral hydrate and chloral alcoholate. These compounds are considered by some chemists as molecular compounds, but if chloral and alcohol pre-existed in the alcoholate, the products of the action of phosphorus pentachloride ought to be identical with those which each of them yields separately, viz., $CCl_3.CHCl_2$ and C_2H_5Cl.

* Deut. Chem. Ges. Ber., 1871, 101.

But if chloral alcoholate is a real compound, or the *monethylic ether of trichlorethylidene glycol*, $\begin{array}{l} CH\begin{cases} OC_2H_5 \\ OH \end{cases} \\ | \\ CCl_3 \end{array}$, then, according to a general difference which the author has observed between ethoxyl and hydroxyl, the action of phosphorus pentachloride must be simply that OH is replaced by Cl, as experiment has proved.

The author therefore considers both this body and choral hydrate as real compounds, the latter being the glycol of trichlorethylidene, $\begin{array}{l} CH(OH)_2. \\ | \\ CCl_3 \end{array}$

The boiling points of the hydrate (95°) and of the alcoholate (115°) ought, according to analogy, to be higher than that of the above-described chlorinated product, which without doubt is a real compound; but these temperatures, as determinations of the vapour-density have shown, are not the real boiling points, but the temperature of dissociation.

The decomposition of chloral hydrate into water and chloral is quite similar to the decomposition of secondary alcohols, as amylene-hydrate, which easily splits up into water and amylene. In the same manner malic and citric acids, which at the same time are secondary alcohols, are decomposed by heat into water and non-saturated acids. Chloral hydrate undergoes this decomposition much more easily, because it contains the two OH groups in close neighbourhood, both being combined with the same carbon-atom. Many chemists doubt the existence of such compounds; but although we do not know many of them at present, there is no theoretical reason why compounds containing more than one hydroxyl combined with the same carbon-atom should not exist, the less so as the corresponding ether groups up to the number of four, can combine with one carbon-atom, forming the stable compounds—

$$CH_3(OC_2H_5),\ CH_2(OC_2H_5)_2,\ CH(OC_2H_5)_3,\ C(OC_2H_5)_4.$$

The stability of groups like

$$CH(OH)_2 \qquad C(OH)_3 \qquad CH_2(OH)_2,$$

depends, according to Baeyer, on the neighbourhood of other negative carbon groups; thus glyoxylic acid, $\begin{array}{l} COH \\ | \\ CO.OH \end{array}$ and chloral, $\begin{array}{l} COH, \\ | \\ CCl_3 \end{array}$ which contain the similar groups CO.OH and CCl_3, one of which can be easily

transformed into the other, combine readily with water, whilst aldehyde, $\begin{array}{l}COH,\\ |\\ CH_3\end{array}$ does not possess this property.

Similar compounds are formed by the combination of water with the higher chlorinated and brominated ketones

$$C_3H_2Cl_4 + 4H_2O.$$
$$C_3H_2Br_2Cl_2O + 4H_2O.$$
$$C_3Cl_6O + H_2O.$$

The author believes that, on taking the phenomena of dissociation into consideration, it will be found more and more difficult to give a definition of the term "molecular compounds."

C. S.

Combination of Chloral with Alcohols and Amides. By OSCAR JACOBSEN.*

CHLORAL brought in contact with alcohols of the ethylic series forms crystalline compounds very similar to the ordinary alcoholate. The melting and boiling points of the compounds obtained are given, together with fresh observations for the hydrate and ethylalcoholate.

	Melting point.	Boiling point.
Chloral hydrate, $C_2HCl_3O.H_2O$	50°—51°	99°
Chloral methylate, $C_2HCl_3O.CH_4O$..	50°	106°
Chloral ethylate, $C_2HCl_3O.C_2H_6O$ ..	56°—57°	115°—117°
Chloral amylate, $C_2HCl_3O.C_5H_{12}O$ ..	56°	145°—147°
Chloral cetylate, $C_2HCl_3O.C_{16}H_{34}O$ ..		

Concentrated sulphuric acid decomposes these compounds with production of chloral. The alcohols of the aromatic series do not unite with chloral.

On bringing chloral in contact with *acetamide* and *benzamide*, crystalline compounds are formed whose formulæ are $C_2HCl_3O.C_2H_5ON$ and $C_2HCl_3O.C_7H_7ON$ respectively. On adding chloral to a saturated solution of *urea*, combination takes place: $C_2HCl_3O.COH_4N_2$ being produced when the urea is in excess, $2(C_2HCl_3O).COH_4N_2$ when the chloral is in excess. The latter body is also obtained by heating dry urea with chloral to 100°. These different amido-compounds are not attacked by dilute acids; heated with alkaline solutions, they break up, with formation of the same products that the constituents would yield by themselves. Chloral-acetamide, for instance, gives with potash-solution, chloroform, ammonia, and potassium acetate and formate.

W. H. D.

* Ann. Ch. Pharm., clvii, 243.

Some derivatives of Acetophenone. By A. EMMERLING and C. ENGLER.*

SECONDARY ethylbenzene alcohol $C_6H_5CH(OH).CH_3$ is obtained in a similar manner to Linnemann's benzhydrol, by hydrogenising acetophenone in alcoholic solution, by means of sodium amalgam. It can be obtained in crystals an inch long, which melt at 120°, and can be distilled, with partial decomposition, by heating to above 200°. By the action of phosphorus pentachloride on the alcohol, chlorethylbenzene, $C_6H_5.CHCl.CH_3$ is produced; an oily liquid, which is not decomposed by water at the ordinary temperature, but is acted on by alcoholic potash.

By heating secondary ethylbenzene alcohol with zinc chloride for some time, water is separated, and a liquid obtained, which, besides benzene, contains a small quantity of a body boiling from 144° to 150°, whose properties agree with those of cinnamene (styrol) from storax. Cinnamene appears also to be produced by the action of alcoholic potash on the above-mentioned chlorethylbenzene. From its synthesis, the constitution of cinnamene might be represented by $C_6H_5.CH{=}CH_2$. It might be regarded as phenylethylene, and might perhaps be produced by the action of sodium on a mixture of bromethylene and bromobenzene.

Bromine attacks acetophenone at ordinary temperatures, forming two derivatives, which can be separated by their differing solubility in alcohol. Acetobromophenone $C_6H_4Br.CO.CH_3$ dissolves in dilute alcohol, and can be obtained therefrom in leafy crystals, which melt at 50°. Potassium chromate and sulphuric acid convert it into bromobenzoic acid, an evidence of the existence of the bromine in the phenyl nucleus. Bromacetophenone $C_6H_5.CO.CH_2Br$ is left undissolved by alcohol in the form of a syrup, which solidifies after a time. By treatment with chromic acid, bromine is set free, and benzoic acid produced; at the same time, bromobenzoic acid is formed in small quantity, an indication of impurity in the bromacetophenone.

W. H. D.

On Blue Chamomile Oil. By J. KACHLER.†

THE author being in possession of a quantity of this oil, has examined it with reference to its composition, and its relation to the blue galbanum oil of Mössner.‡

That it is a mixture, was at once evident on rectifying the crude oil, previously distilled in a current of steam; it began to boil at 105°, and

* Deut. Chem. Ges. Ber., iv, 147.
† Deut. Chem. Ges. Ber., iv, 36.
‡ Ann. Ch. Pharm., cxix, 257.

between this and 188° a small quantity—206 grms. crude oil gave 9 grms.—of a faintly blue oil, smelling strongly of chamomile passed over; and between 188° and 255° a second fraction of 17 grms. of a somewhat darker colour, was obtained. The magnificent blue vapour which characterises this oil, was first formed above 255°; the temperature then rose slowly to 295°, and 87 grms. distilled over. The portion distilling above 295° was still blue, but more syrupy. The temperature then rose above that at which a mercury thermometer could be employed, the vapour became violet, and 43 grms. of a thickish, but still blue oil, were obtained. Finally, there remained in the retort 41 grms. of a brown tar.

All these fractions had an acid reaction and were, therefore, washed with potash-solution; the wash-water was acidified with sulphuric acid and extracted with ether; and the strong, unpleasant smelling residue remaining after distilling off the ether, was dissolved in water, saturated with ammonia, and converted into a silver salt.

The analysis of this salt leads to the conclusion, that the acid is *rutic* or *capric* acid, $C_{10}H_{20}O_2$.

(Obtained.. 43·1 per cent. C., 6·5 per cent. H., 38·4 per cent. Ag.
Required .. 44·2 per cent. C., 6·8 per cent. H., 38·7 per cent. Ag.)

From the first two fractions, a portion was separated after repeated rectification, boiling at 150°—168°, which had a composition indicated by the formula $C_{16}H_{10}O$.

(Obtained.. 79·1 per cent. C., 10·8 per cent. H.
Required .. 79·0 per cent. C., 10·5 per cent. H.)

The analysis of the portions of higher boiling point (165°—185°) indicated increasing amounts of carbon and hydrogen, the mean of several determinations being 82·93 per cent. C., and 11·10 per cent. H.; probably due to the presence of a $C_{10}H_{16}$ hydrocarbon isomeric with oil of turpentine. Bizio's* analyses also lead to the same conclusion.

The blue fraction, after washing and drying over calcium chloride, was repeatedly rectified, and the various portions analysed. The portions of lower boiling point are, as is plainly shown by their colours, the least pure. That obtained between 270°—300° has the purest colour, a magnificent azure-blue, similar to that of an ammoniacal copper solution. From numerous analyses of this, and from the results obtained by Bizio and Bornträger,† it is evident that this body is an isomeride, or polymeride of camphor.

$C_{10}H_{16}O$		Bornträger.			Bizio.	Kachler.					
					300°	275°	281°	287°	(287—288°)		289°
C..	79·0	79·85	79·81	79·86	78·11	79·8	79·0	78·92	78·5	78·4	79·5
H..	10·5	10·60	10·69	10·89	10·69	10·4	10·3	10·37	10·7	10·7	10·5

* Wien. Akad. Ber. xliii, [2], 292.
† Ann. Ch. Pharm., xlix, 243.

Vapour-density determinations were also made, but the results are inaccurate as the oil is partly decomposed when heated for some time above 310°—320°; nevertheless, the experiments prove that the molecular formula is certainly double, and probably treble the empirical camphor formula, $C_{10}H_{16}O$.

A comparison of the properties of this portion of the chamomile oil, which the author holds to be pure, with those of the corresponding fraction of the oil obtained by distillation of galbanum by Mössner, shows them to be identical except in composition which differs considerably.

	Blue Chamomile Oil, 281°—289°.	Blue Galbanum Oil, 289°—290° (Mössner).
C =	79·25 per cent.	83·74 per cent.
H =	10·40 ,,	11·43 ,,

Kachler finds, however, that the galbanum oil is a very variable mixture according to the temperature at which the resin is distilled. It contains varying quantities of a colourless hydrocarbon, which possesses the turpentine formula, and may be driven off by heating for two or three days at 230°—250°. This hydrocarbon when purified by distillation, is not identical with the colourless, limpid, turpentine-like galbanum oil obtained by distillation of galbanum in a current of steam. It is less limpid, has a perfectly different, unpleasant odour, and boils at 240°—250°; whereas, the latter boils at 160°—165°. It is probable that the high percentage of carbon in Mössner's blue oil, is due to an admixture of this hydrocarbon. Kachler found, that the blue galbanum oil, after purification from this body &c., gave 79·07 and 80·8 per cent. C., and 10·42 and 10·4 per cent. of H.; numbers agreeing well with the camphor formula.

On treating chamomile oil with potassium and with phosphoric anhydride in the same way as Mössner treated galbanum oil, the behaviour of the two oils was found to be identical, and the products obtained were of the same composition.

Products of the treatment with potassium:—

	From Galbanum Oil.			From Chamomile Oil.	
	$nC_{10}H_{16}$.	Mössner (255°).		Kachler (255°).	Kachler (250°—255°).
C	88·6	88·7	88·8	88·0	88·1
H	11·4	11·3	11·1	11·4	11·8

The vapour-density determined by Dumas' method, was 14·8; that calculated for $3(C_{10}H_{16})$ being 14·1.

Products of the action of phosphoric anhydride:—

$n(C_{10}H_{16}O) - n(H_2O) = n(C_{10}H_{14})$.		From Galbanum oil. Kachler.	From Chamomile oil. Kachler.
C	89·6	89·2	88·8
H	10·4	10·4	10·8

The author then remarks that, bearing in mind the extreme difficulty of preparing such bodies in the pure state, he would not have considered the analytical results obtained with the two oils perfectly conclusive in favour of their identity, were it not for some other characteristic reactions which seem to remove all doubt. On adding an ethereal bromine solution to a dilute ethereal solution of the product from the treatment of the blue chamomile oil with potassium, the liquid becomes, after a short time, azure blue.—This colour is not persistent; on the evaporation of the ether, which must have been employed saturated with water, it turns green, and finally brown. The product from galbanum oil and also the products of the action of phosphoric anhydride on the two oils, all give exactly the same reaction.

On agitation with nitric acid, sp. gr. 1·25, a similar reaction is observed. The brownish colour at first produced, soon passes into a deep violet; afterwards oxidation takes place, and the colour disappears.

H. E. A.

On Indian Oil of Geranium. By Oscar Jacobsen.*

The commercial oil of geranium investigated was a greenish-yellow liquid, having an agreeable smell of roses, and a feebly acid reaction. It had a sp. gr. of 0·887 at 20°, yielded no deposit when cooled at from 10° to 15°; and did not act on polarised light. Another sample of oil had at 20° a sp. gr. = 0·910; but was adulterated with 20 per cent. of fatty oil.

Fractionally distilled, about 8 per cent. came over between 90° and and 120° (this was alcohol, which was not present in the second sample); the thermometer then rose quickly, the greater part distilling over between 210° and 240°. At 250° a thick brown residue was left. Traces of copper were present in both samples of oil. The portion distilling below 210° contained valeric acid.

By repeated fractional distillation of the product, which came over between 210° and 240°, a liquid was obtained, boiling at 232°—233°, called by the author *geraniol*, whose analysis gave numbers agreeing with the formula $C_{10}H_{18}O$.

Geraniol is a colourless, strongly refracting liquid, which does not solidify at − 15°, and does not act on polarised light. Its density is 0·8851 at 15°. With alcohol and ether it mixes in all proportions. With calcium chloride, it forms the compound $CaCl_2.2C_{10}H_{18}O$.

* Ann. Ch. Pharm., clvii, 232.

Fusing potash produces valeric acid by its action on geraniol. By oxidation with a cold, neutral solution of potassium permanganate, geraniol yields valeric acid; in addition, fatty acids poorer in carbon, especially acetic acid, when the solution is allowed to become heated.

With a hot solution of potassium chromate and sulphuric acid the principal product is acetic acid; valeric and succinic acids are also formed.

Nitric acid produces nitrobenzene, hydrocyanic acid, oxalic acid, and a resin, but no analogue of camphoric acid.

By passing gaseous hydrochloric acid through geraniol, or by heating the latter body for some hours to 80°—90° with strong aqueous hydrochloric acid, *geraniol chloride* $C_{10}H_{17}Cl$ was obtained as an oily liquid, which decomposed on distillation. The chlorine appears to be easily movable; silver nitrate precipitates it completely from the alcoholic solution of the chloride. Potassium bromide and iodide convert geraniol chloride in alcoholic solution, at the ordinary temperature into the *bromide* $C_{10}H_{17}Br$, and the *iodide* $C_{10}H_{17}I$. The cyanide, sulphocyanate, and various compound ethers, can be obtained in an analogous manner.

Geraniol oxide $C_{20}H_{34}O$ was obtained by heating the chloride with geraniol, with water, or with alcoholic potash. The *sulphide* $C_{20}H_{34}S$ was obtained by the action of alcoholic potassium sulphide on geraniol chloride.

Geraniol, like its isomeride, borneol, appears to function as a monatomic alcohol; the fact that geraniol and its derivatives are liquids and inactive towards polarised light, constitutes a physical difference between them and borneol.

By distilling geraniol with zinc-chloride or phosphoric anhydride, a liquid hydrocarbon *geraniene*, boiling at 162°—164°, was produced. The formula of geraniene is $C_{10}H_{16}$; its vapour-density, taken at 237° = 4·93. It forms with hydrochloric acid a liquid chlorhydride; but no hydrate was obtained on treating the hydrocarbon according to Wiggers's method of preparing terpine.

W. H. D.

On the Separation of the Ethyl Bases by means of Oxalic Ether. By A. W. Hofmann.*

This well-known method, which the author discovered some time ago (Proc. Roy. Soc. xi, 66), is best carried out in the following way:—The mixture of bases, after having been well dried over caustic potash, is placed in a flask which is connected with a reversed condenser and provided with a tap funnel, by means of which perfectly dry oxalic

* Zeitsch. f. Chem. [2], vii, 38.

ether is added drop by drop. For 100 grms. of the mixed bases 150 grms. of oxalic ether are sufficient. After cooling, the contents of the flask solidify to a soft crystalline mass, whilst still warm is placed in a glazed autoclave and heated in the water-bath for several days. The vessel is then connected with a condenser, and heated in a salt-bath as long as alcohol and triethylamine come over. By neutralising the distillate with hydrochloric acid and evaporating on the water-bath, triethylamine hydrochloride is left behind as a fibrous, crystalline, not deliquescent mass.

The residue in the autoclave, which consists of a half liquid and half solid mass, is cooled in a freezing-mixture and then pressed between linen cloth, by which means *diethyl oxamide*, $C_2O_2[N(C_2H_5)H]_2$, is left behind, which is purified by crystallising it from hot water. From this compound pure ethyl amine can any time be obtained by distilling it with caustic potash. The liquid which has passed through the cloth, consisting chiefly of *ethylic diethyloxamate*, $C_2O_2\left\{\begin{matrix} N(C_2H_5)_2 \\ OC_2H_5 \end{matrix}\right.$, is subjected to fractional distillation, whereupon first small quantities of alcohol, triethylamine, and diethyloxamide pass over, then between 250°—254° pure ethylic diethyloxamate, and at last oxalic ether. The diethyloxamate is kept and used for the preparation of diethylamine when required. The mother-liquor from the diethyl oxamide yields on distillation with caustic potash a mixture of ethylamine and diethylamine, which can be used for lecture experiments. The fractions distilling below and above ethylic diethyloxamate are employed in a fresh operation.

For the preparation of the three bases the author used the crude ethylic chloride, which is obtained as a bye-product in the manufacture of chloral. He found that diethylamine is always formed in the largest quantity and obtained by the above-described process several kilogrammes of pure ethylic diethyloxamate. C. S.

Preparation of Guanidine. By A. Bannow.*

In Erlenmeyer's synthesis of guanidine, by the action of chloride of cyanogen on ammonia, equivalent to cyanamide and ammonium chloride, the author finds that the chloride can be conveniently replaced by the iodide of cyanogen. The solubility of ammonium iodide in alcohol appears to hasten the formation of guanidine. Iodide of cyanogen with three times its weight of alcoholic ammonia (of 10 per cent.), heated in a sealed tube in the water-bath for three hours, gave almost the theoretical quantity of guanidine salt, in a nearly pure state. W. H. D.

* Deut. Chem. Ges. Ber., iv, 161.

On the Action of Sulphur Chloride upon Aniline in Presence of Carbon Bisulphide. By AD. CLAUS and W. KRALL.*

BY acting upon aniline with *crude* sulphur chloride, which, to moderate the violent reaction, was diluted with carbon bisulphide, the authors obtained a product which, as they believed, contained some new compounds. But on repeating their experiments with *pure* sulphur chloride, they found that only well known bodies are formed, which in their former experiments were further acted upon by the excess of chlorine contained in the crude sulphur chloride, and that the carbon bisulphide takes part in the reaction, which is completed in two stages.

First sulphocarbanilide, aniline hydrochloride, and free sulphur are formed, thus—

$$4C_6H_7N + 2SCl + CS_2 = C_{13}H_{12}N_2S + 2(C_6H_7N.HCl) + 3S.$$

In the second stage, the excess of sulphur chloride acts upon the sulphocarbanilide, exactly as Hofmann has shown that iodine does, producing triphenyl-guanidine and phenylic mustard oil:

$$2C_{13}H_{12}N_2S + 2SCl = C_{19}H_{17}N_3.HCl + C_7H_5NS + HCl + 3S.$$

C. S.

Action of Zinc Chloride, Nitrous Acid, Chloride of Lime and Hydrochloric Acid, on Morphine; and of Zinc Chloride on Papaverine. By E. L. MAYER.†

Action of Zinc chloride on Morphine. A solution of zinc chloride, boiling at about 200°, was allowed to cool to 110°, and then mixed with a hot saturated solution of morphine hydrochloride. The liquid was then heated for $1\frac{1}{2}$ hours to 120°. Apomorphine was recognized as a product of decomposition at this temperature, by its analysis, and by its reactions and physiological effects. The formation of apomorphine is preceded by that of a body not yet examined; but probably differing from morphine by $-\frac{H_2O}{2}$. If the zinc solution be heated to 170°, no apomorphine is obtained, but another basic substance, not yet investigated.

Action of Nitrous Acid on Morphine. Nitrous acid, prepared by reducing nitric acid with arsenious oxide, was passed rapidly through water, which held about $\frac{1}{30}$ its weight of pure morphine suspended. The morphine soon dissolved, the liquid becoming dark. When only a few flakes of morphine were left undissolved, the liquid was quickly

* Deut. Chem. Ges. Ber., iv, 99.

† Deut. Chem. Ges. Ber., iv, 121.

filtered, and set aside. After 24 hours' standing, about 50 per cent. of the morphine employed had separated in the form of reddish-yellow crystals. This separation is increased by agitating or warming the liquid. The crystals washed first with water, and then with cold alcohol, were dried over sulphuric acid. The results of several analyses led to the formula, $C_{17}H_{18}(NO)NO_3 + H_2O$. It is called for the present "body A." Heated to 125° it loses 5·40 per cent. H_2O, leaving $C_{17}H_{18}(NO)NO_3$. On boiling with water, decomposition took place, attended by evolution of an odourless gas. A deposit (D) remains undissolved after continued boiling; it is removed by filtration from the liquid, which contains in solution a substance (C) not yet obtained in the pure state. The body D gave on analysis numbers which would agree equally well with the formula $C_{17}H_{19}NO_4$ or with $C_{17}H_{18}NO_4$. With hydrochloric acid it evolves chlorine, and apparently another gas. When the substance A is added to a cold mixture of one-third concentrated sulphuric acid, and two-thirds water, a violent disengagement of gas (apparently nitric oxide) takes place. The body D behaves in a similar manner. At the same time another substance is formed, whose composition, when dried at 125°, agrees with either of the formulæ $2(C_{17}H_{19}NO_3)H_2SO_4$, or $2(C_{17}H_{18}NO_3)H_2SO_4$.

Action of Chloride of Lime and Hydrochloric Acid on Morphine.—When solution of chloride of lime is added to morphia dissolved in an excess of dilute hydrochloric acid, greenish-white flakes are deposited, which do not disappear on addition of more hydrochloric acid. These flakes were dissolved in boiling alcohol, the alcoholic solution precipitated by water, and the precipitate dissolved in ether. On distilling off the ether, an oil is left behind, which becomes solid after about ten days' standing over oil of vitriol. Its analysis gave 40·52 per cent. carbon, 3·37 per cent. hydrogen, and 20·85 per cent. chlorine, numbers which would be given by $C_{17}H_{16}Cl_3NO_{10}$.

Papaverine and Zinc chloride.—Hydrochloride of papaverine heated with solution of zinc chloride, appears to lose a molecule of water, with formation of a basic compound, whose hydrochloride had the composition $C_{40}H_{42}N_2O_7.2HCl$.

$$2C_{20}H_{22}NO_4 - H_2O = C_{40}H_{42}N_2O_7.$$

Papaverine, by further treatment with zinc chloride, and by treatment with chloride of lime, appears to yield substances similar to those obtained from morphine under like conditions.

W. H. D.

Action of Nitrous Acid on Urea in aqueous solution. By A. Claus.*

The decomposition of urea on warming its aqueous solution with

* Deut. Chem. Ges. Ber., iv, 140.

nitrous acid is at present represented in two different ways, as shown by the following equations:—

$$\text{(I)}\quad CH_4N_2O + N_2O_3 = CO_2 + 2N_2 + 2H_2O;$$
$$\text{(II)}\quad 2CH_4N_2O + N_2O_3 = (NH_4)_2CO_3 + 2N_2 + CO_2,$$

the first of which is to be found in most text-books; the second is that given by Wöhler and Liebig many years ago. The author, having recently investigated the action more exactly, finds that both modes of representation are correct under certain circumstances. When nitrous acid (1 mol.) is added to solution of urea (2 mol.) in the cold, and the mixture is then heated, decomposition takes place as represented by equation (II); carbon dioxide and nitrogen are evolved in the proper proportions, and the residual liquid contains ammonium carbonate only. When, however, nitrous acid is gradually added to a hot solution of urea, in the above proportions, the same quantities of carbon dioxide and nitrogen are evolved as before, but nearly half the urea remains undecomposed. In this case the decomposition evidently takes place according to equation (I), only half of the urea taking part in the reaction; but the author has noticed that the reaction is never *perfectly* expressed by this equation, some ammonium carbonate being always found in solution together with the unaltered urea. These apparently contradictory facts are explained in the most simple manner by the observation made long ago by Wöhler and Liebig (*Ann. Chem. Pharm.* xxvi, 261) that urea (2 mol.) and nitrous acid (1 mol.) react upon each other in the cold, forming cyanic acid and ammonium nitrite. When, therefore, the two substances are brought together in the cold, the first reaction is as follows:—

$$2CH_4N_2O + N_2O_3 + H_2O = 2NH_4NO_2 + 2CNHO;$$

on warming the solution, further changes take place, the ammonium nitrite being resolved into nitrogen and water, and the cyanic acid reacting with water to form ammonium carbonate and carbon dioxide, thus:—

$$2NH_4NO_2 = 2N_2 + 4H_2O; \text{ and}$$
$$2CNHO + 3H_2O = (NH_4)_2CO_3 + CO_2.$$

When, on the other hand, the nitrous acid is added by degrees to a hot solution of the urea, a small quantity of urea at once undergoes the above changes with the first portion of acid added, whilst further portions of acid coming in contact with the newly-formed ammonium carbonate as well as with urea, act simultaneously upon both these substances, a part acting upon the ammonium carbonate to form carbon dioxide, nitrogen, and water, and the remainder decomposing urea in the manner described. Under these conditions some of the urea must obviously remain undecomposed.

The decomposition expressed in equation (II) can be realised only by adding the whole of the nitrous acid to the urea in the cold and then heating, or by adding, together with the nitrous acid, an equivalent quantity of a stronger acid. In the latter case it is a matter of indifference whether the heat be applied before or after mixing.

J. R.

Decomposition of the so-called Sulpho-ureas by Nitrous Acid. By A. CLAUS.*

THE author employs in his experiments a solution of nitrous ether in alcohol (obtained by saturating cooled absolute alcohol with nitrogen trioxide), having ascertained that such a solution, when preserved in closed vessels in the cold, acts in precisely the same way as freshly-prepared nitrogen trioxide passed into alcoholic solutions.

Diphenylsulphocarbamide treated with this solution in the cold is instantly decomposed, evolving torrents of gas, which consists chiefly of nitric oxide, and is certainly free from carbon dioxide and oxysulphide. Some time after the termination of the experiment, the liquid, which is turbid at first, becomes perfectly clear, and a quantity of free sulphur is deposited, exactly equal to half the amount contained in the sulphocarbamide employed. The alcoholic liquid then contains phenyl sulphocyanate and triphenylguanidine, nearly in the calculated proportion. The decomposition appears to be represented by the equation—

$$2C_{13}H_{12}N_2S + N_2O_3 = C_{19}H_{17}N_3 + C_6H_5.CNS + S + H_2O + 2NO,$$

according to which, the action of nitrous acid in alcoholic solution is perfectly analogous to that of iodine, chloride of sulphur, &c.

The author has also examined the action of the above reagent on *sulphocarbamide* and on the isomeric compound, *ammonium sulphocyanate*, hitherto without arriving at any definite results. He has observed the remarkable fact that ordinary urea is not acted upon by alcoholic nitrous acid. Urea treated with a large excess of the reagent dissolves without decomposition; the solution does not evolve gas, even on standing for weeks in closed vessels, and when afterwards evaporated over the water-bath deposits unaltered urea.

J. R.

On Phenylic Xanthamide. By A. W. HOFMANN.†

THIS compound is formed, together with xanthic acid and free sulphur, by acting upon aniline with ethylic disulpho-carbon sulphide (Debus's ethylic bioxysulphocarbonate)

* Deut. Chem. Ges. Ber., iv, 143.

† Zeitschr. f. Chem. [2], vii, 37, from Deut. Chem. Ges. Ber., iii, 172.

$$\left.\begin{matrix}(C_2H_5)_2\\(CS)_2\end{matrix}\right\}O_2S_2 + \left.\begin{matrix}C_6H_5\\H_2\end{matrix}\right\}N = S + \left.\begin{matrix}CS(C_6H_5)HN\\C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}CSO_6.$$

A portion of the xanthic acid is further acted upon by an excess of aniline present, diphenylic sulphur urea being formed—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}CS_2O + 2\left.\begin{matrix}C_6H_5\\H_2\end{matrix}\right\}N = \left.\begin{matrix}CS\\(C_6H_5)_2\\H_2\end{matrix}\right\}N_2 + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + H_2S.$$

The phenylic xanthamide obtained by this reaction is identical with that previously described by the author. It forms triclinic crystals, which are more soluble in alcohol than sulphur urea.

C. S.

A new Solvent for Indigotin. By A. A. DE AGUIAR and ALEX. BAYER.*

THE authors first call attention to the difficulty of obtaining crystallised indigotin in the pure state, chiefly owing to its insolubility in the ordinary solvents; boiling creosote and phenol, which dissolve it in small quantity, deposit it in a flocculent state on cooling. They find, however, on boiling finely powdered commercial indigo with aniline, that the colouring matter readily dissolves, yielding a deep blue solution, which, if filtered hot and set aside for some hours, deposits almost the whole of the indigotin in the crystalline state. When required very pure, it should be again crystallised from aniline, and the crystals washed with alcohol and dried. As thus obtained it is chemically pure, has a brilliant coppery lustre, and rivals in appearance that prepared by sublimation.

The authors, in their endeavours to find other solvents that might be employed in place of aniline, observed that benzol and chloroform dissolve indigotin in small quantity, and deposit it in a flocculent state on cooling. Alcohol and ether at their boiling temperatures also dissolve it in small quantity.

C. E. G.

* Ann. Ch. Pharm., clvii, 366.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XVI.—*On some Saline Compounds of Cane-Sugar.*

By C. Haughton Gill.

Peligot has described* a compound of cane-sugar and salt, to which he ascribed the formula $C_{24}H_{42}O_{21}NaCl$ (C = 6 H = ·5 O = 8), which requires 14·92 per cent. of sodic chloride; this indicates the replacement of 9 parts of water by 58·5 parts of sodic chloride. Blondeau de Carrolles subsequently examined a similar compound, to which he ascribed the formula $C_{24}H_{20}O_{20},NaCl,3HO$; this includes water of crystallisation, of which Peligot makes no mention. Subsequently Mitscherlich denied the existence of the body, and Hochstetter mentioned that other chemists had failed to obtain it. Others in France and Germany having incidentally thrown doubts on the existence of any saline compounds of cane-sugar, it became of interest to me, for technical reasons, to examine into the question, and to ascertain whether Peligot's statements were really unfounded.

Having obtained some positive results, I beg to lay them before the Society, for though of little interest in themselves, their publication may prevent the necessity of some other worker wasting so much time on an ungrateful subject.

Being at first unsuccessful in preparing Peligot's compound by the method which he describes, I boiled a solution of sugar with an excess of salt for some time, filtered, and set aside the apparently uncrystallisable syrup, while other experiments were undertaken. At the end of some months, a few small, not very transparent, but individually distinct crystals, had formed. They were drained, rinsed, and pressed.

·5744 grm. lost ·045 grm. water by drying for 74 hours at 60°—120° C., and when ignited with hydric sulphate left ·1304 grm. sodic sulphate.

These numbers lead to the formula $2C_{12}H_{22}O_{11}.3NaCl.4H_2O$.

	Calculated.	Found.
$C_{12}H_{22}O_{11}$ (by difference) ..	73·43	73·47
NaCl	18·84	18·70
H_2O.....	7·73	7·83
	100·00	100·00

This compound, of an unexpected composition, having been obtained,

* Ann. Ch. Pharm. xxx, 71.

a number of solutions of sugar with various proportions of different salts, were made up and set aside to crystallise spontaneously in a dry air-space, or in the gentle and regular warmth of a sugar-house working floor. Where crystals were not obtained by these means, a more rapid evaporation was tried, or an alcoholic solution was slowly evaporated, and in many cases these and other methods were tried with liquids, neutral, alkaline, and faintly acid. The salts employed were, the chlorides of potassium, sodium, lithium, and ammonium, the bromides of potassium, and sodium, and the iodides of potassium, sodium, lithium and ammonium. In each case, four solutions were prepared, having one, two, three, and four molecules of the salt to the double molecule of sugar $2C_{12}H_{22}O_{11}$.

None of the potassium salts gave compounds of a definite composition. The mixture containing the chloride in the smallest proportion, gave crystals of pure sugar; those containing the two largest proportions gave a crop of pure potassic chloride. From the solution containing $2KCl$ to $2C_{12}H_{22}O_{11}$, *anhydrous* crystals containing from 1·3 per cent. to 19·6 per cent. of potassic chloride, slowly separated, leaving behind a mother liquid of the consistency of treacle.

The solutions containing potassic bromide behaved in a very similar manner, giving crystals often very clear and sharp, and sometimes five or six mm. in extreme dimensions, but always *anhydrous* and of irregular composition. Different specimens contained such proportions of potassic bromide as 24·8, 19·15, 16·17, 12·0, 7·56, 28·15 and 22·3 per cent. In appearance the crystals could not be distinguished from those of pure sugar. The solutions containing potassic iodide evaporated to very thick sticky masses, sometimes containing a number of minute crystals which could not be separated from the mother liquor.

The sodium salts gave more definite results. In the case of the chloride, the solution containing least salt first gave crystals of pure sugar, and then, on further concentration, deposited crystals which are doubtless the same as those of the compound examined by Peligot, and are identical with those obtained from the liquid containing the next higher proportion of salt, viz., $NaCl$ to $C_{12}H_{22}O_{11}$.

This compound crystallises in prisms terminated by pyramids; it deliquesces only in very moist air—loses no water in a dry vacuum at ordinary temperatures, but gives off the whole of its water of crystallisation, amounting to 8·25 per cent. by long exposure to a temperature of 60°—70° C. It is very soluble in water, less so in spirit. From its solution in hot spirit of 85 per cent., *anhydrous* crystals containing from 5 to 10 per cent. of sodic chloride are deposited on cooling or slow evaporation, and these, on being again crystallised from spirit, give a crop of pure sugar. When ether is added to its solution in spirit of not more than 75 per cent., an oily layer is formed

at the bottom of the vessel, and in this crystals form, and continue to grow for eight or ten months; these are hydrated and definite in composition. They are thin, hard, and transparent, and of exactly the same composition as those obtained by recrystallisation of the original crop from water or, what is better, spirit of 10 per cent.

1·4011 grm. ether deposited compound lost ·1157 water by drying for 152 hours at 65° C., and gave ·2277 grm. sodic sulphate.

1·0121 grm. which had been recrystallised from water lost ·083 grm. water, and gave ·1641 grm. sodic sulphate.

	Calculated.	Ether deposited crystals.	Re-crystallised from water.
$C_{12}H_{22}O_{11}$ (by difference) ..	—	—	—
NaCl.....	13·4	13·39	13·36
H_2O	8·25	8·26	8·20

These numbers agree closely with those required by the formula $C_{12}H_{22}O_{11}.NaCl.2H_2O$.

Many different preparations of this compound were analysed, some of which were deposited from solutions containing sugar or salt in excess. The crystals were pressed and dried, but not recrystallised.

Found	NaCl ..	13·48	13·5	13·5	13·6	13·35
	H_2O ..	—	—	—	8·0	—

The solutions containing three and four molecules of sodic chloride to the double molecule of sugar, for the most part, first deposited crystals of salt, and then those of the above-described compound; and hitherto I have been unable to satisfactorily determine the conditions necessary for the production of the body described at the beginning of this paper. I have only once succeeded in preparing that compound since the first lot of accidentally formed crystals, and on this solitary occasion there had been a continuance of very cold weather during the whole period of crystallisation. This second lot of crystals gave the following numbers on analysis:—

1·3005 grm. lost ·1004 water, and gave ·2927 grm. sodic sulphate, or 7·72 per cent. water, and 18·55 per cent. sodic chloride, which numbers show it to be the same body as that previously analysed.

The solutions containing sodic bromide can hardly be made to crystallise at all. A small quantity of minute confused crystals were deposited after some months from the solution containing 3NaBr to $2C_{12}H_{22}O_{11}$; these, when pressed and dried over oil of vitriol, gave numbers which would point to a formula $NaBr.C_{12}N_{22}O_{11}.1\frac{1}{2}H_2O$, but it is more probable that when pure it is similar in composition to the analogous compound of sodic chloride: unless, like the iodine compound next to be described, it differs from the corresponding chlorine compound in respect to water of crystallisation.

	Calculated for $C_{12}H_{22}O_{11}.NaBr.2H_2O$.	Found.	Calculated for $2C_{12}H_{22}O_{11}.2NaBr.3H_2O$.
$C_{12}H_{12}O_{11}$ ..	—	—	—
NaBr	21·4	22·07	21·82
H_2O	7·48	5·49	5·72

The solutions containing sodic iodide give crystals of definite and constant composition with remarkable ease. These crystals always have the same composition whatever the proportions of the constituents in the mixture, unless one be in such large excess that it can in part crystallise out before the liquid becomes saturated with the compound. The solutions containing a moderate excess of sodic iodide yield the best crystals and quickest growth. They can be recrystallised as often as desired from water or dilute spirit, without suffering decomposition, forming large transparent crystals even from small quantities of solution —70 c.c. of the saturated solution when allowed to evaporate spontaneously over oil of vitriol often giving crystals more than an inch long and half an inch thick, resembling Rochelle salt in general appearance.

For the following analysis a portion, which had been three times crystallised from water, was used :—

(*a.*) ·7949 grm. crushed and dried over oil of vitriol gave ·472 grm. silver iodide.

(*b.*) 1·5307 grm. lost ·0683 by drying 64 hrs. at 60°—100° C., and gave ·275 grm. sodic sulphate.

These numbers agree with the formula $2C_{12}H_{22}O_{11}.3NaI.3H_2O$.

	Calculated.	Found.	
		a.	*b.*
NaI	37·88	37·9	37·87
H_2O	4·54	—	4·46

Other crystals from solutions containing either a large excess of sugar, or of sodic iodide, or which had been crystallised from spirit, gave the following numbers, which show that this body forms under very various conditions :

NaI ..	37·85	37·76	38·3	38·4	37·71	37·9
H_2O ..	—	—	—	4·35	—	4·67

When powdered, the crystals lose no water in a dry vacuum, but they lose all at 60° C. without melting, and the dry mass will then bear a temperature of about 120° C. without decomposition. Fresh crystals melt at about 90° C., and cannot afterwards be dried. They are slightly deliquescent in very moist air, soluble in 1·5 times their weight of water at ordinary temperatures, and in an indefinitely small quantity at 100° C. They are soluble in spirit to a less extent, nearly absolute

alcohol causes a separation of sugar. 20 grms. of crystals crushed between paper, but not otherwise dried, dissolved up to 100 c.c., gave a liquid which in a column of 200 mm., rotated a ray of polarised light $\frac{69}{100}$ as much as a plate of right-handed quartz 1 mm. in thickness, while the sugar contained in it (reckoned as pure) would, if brought to the same volume, have caused a rotation of $\frac{70{\cdot}4}{100}$, from which it appears that the rotatory power of sugar is not altered by combining with sodic iodide.

The specific gravity of the crystals themselves is 1,854.

Professor W. H. Miller has been so kind as to examine these and some other crystals for me. His measurements and other observations here quoted. I take this opportunity of expressing my thanks and obligations for Professor Miller's most valuable help.

"Compound of cane-sugar and sodic iodide.

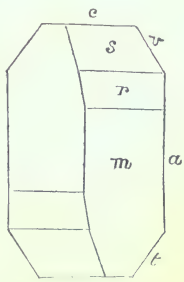
"*Oblique.*—Simple forms, *a* 1 0 0, *c* 0 0 1, *v* 1 0 1, *t* 1 0 $\bar{1}$, *m* 1 1 0, *s* 1 1 1, *r* 3 3 2.

"Angles, measured by the angles between normals to the faces—

c a	85°	20′
c v	54	26
c t	118	53
a m	63	46
c m	87	56
c r	77	29
c s	72	30
v s	58	52

"Cleavage, *c* perfect, *a* less distinct. The forms to which the faces *r*, *s*, *v*, *t*, belong occur but seldom, and the values of the angles they make with *c*, and with one another, are liable to considerable uncertainty.

"*Twins.*—Twin-face *a*. *c* ɔ = 9° 20′.*



"The optic axes are in a plane normal to the plane of symmetry. When seen through the face *a* and the opposite parallel face, in oil, they make with each other an angle of between 114° and 115°. A line bisecting this angle lies between normals to *c* and *a*, making with the latter an angle of about 12°. When the crystal is immersed in oil, so that light is refracted through the faces *c*, *a*, in a plane normal to the edge *ca*, the most refracted ray is found to be polarized in the plane of refraction."

* The *c* ɔ is the letter *c* and a letter *c* turned upside down—a notation that I have found very convenient in expressing the angle between the faces of two crystals constituting a twin crystal.

None of the mixtures containing lithium gave any crystals other than those of sugar; those containing a large proportion of the salt simply dried up to a gummy mass.

The mixtures containing ammonic salts gave no definite compounds. The chloride, when in small quantity, allowed sugar to crystallise out freely; when in large quantity, it hindered crystallisation, but in time allowed the liquids to deposit well formed, isolated, anhydrous crystals, generally opaque, but having the appearance of a definite body. These crystals in fact contained most variable proportions of ammonic chloride, *e.g.*, 7·2, 6·76, 6·7, 0·78, 0·85, and 4·9 per cent.

No results were obtained from the solutions containing ammonic iodide.

These crystals of sugar, containing ammonic chloride, and the equally distinct, though generally smaller ones, containing potassic bromide, and those deposited from a hot alcoholic solution of the lower salt compound, must, I imagine, be built up by an *anhydrous* compound of the salt and sugar, isomorphous with sugar itself, crystallising out, together with an excess of the latter.

Professor Miller has examined some of the crystals containing ammonic chloride, and reports as follows :—

"The crystals of the compound of cane sugar and ammonic chloride are not distinguishable in form from those of pure sugar. In consequence probably of the difficulty of removing the syrup from the faces of the crystals, the measurements made by Rammelsberg, Hankel, and Wolff, differ considerably from one another (Rammelsberg, *Handbuch der krystallographischen Chemie*, S. 397), and from measurements made by myself some time ago (Cambridge Philosophical Transactions, vol. vii, p. 209).

"The crystals of sugar and ammonic chloride belong to the oblique system. The simple forms are :—

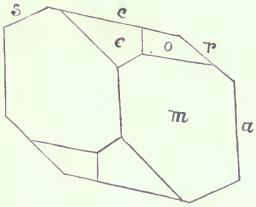
c 0 0 1, a 1 0 0, e 0 1 1, r 1 0 1, s $\bar{1}$ 0 1, m 1 1 0, o 1 1 1.

"As in crystals of pure sugar, the forms to which the faces e, o belong appear to be hemihedral, those faces only being found which are on one side (not always the same) of the plane of symmetry.

"Taking the angle between normals to two faces of a crystal drawn towards the faces from a point in the interior, for the measure of the dihedral angle made by the faces, Wolff's observations give :—

$c\ a$	=	76°	30′
$a\ r$	=	46	15
$a\ s$	=	115	30
$c\ e$	=	40	30
$a\ m$	=	50	46

r o	=	32°	24′
c m	=	81	30
c o	=	43	10
c e	=	40	30
m r	=	64	4
m s	=	105	48
a e	=	79	46
m o	=	38	20
a o	=	54	16



"The differences between these angles and those of the crystals of sugar containing ammonic chloride, are not larger than the differences between the angles obtained for pure sugar by the observers mentioned above."

That the crystals are not simply sugar with adhering ammonic chloride is, I think, shown by their individual perfection, and by the fact that they are deliquescent, whereas neither constituent is so.

The solutions of all the bodies described in this paper, especially those of the lower salt compound, exhibit persistent supersaturation in a remarkable degree. A saturated warm solution, when cooled and shut up in an air-tight vessel with several crystals of the solid body, continues to deposit more of the compound for several months.

It is to be remarked that the sodium salts which give definite compounds are known to crystallise with two molecules of water, when deposited at low temperatures, and that the iodide does so at all temperatures up to 20° C., whereas the corresponding potassium salts are anhydrous, at whatever attainable temperature they may be crystallised.

The composition of the sodic iodide compound makes it seem probable that the true molecular weight of cane sugar should be represented by $C_{24}H_{44}O_{22}$.

I have endeavoured to prepare compounds of sugar with sodic acetate, nitrate, iodate, and rhombic phosphate, but in no case did I get any but anhydrous bodies of indefinite composition.

These experiments were made in Messrs. Martineau's refining laboratory.

XVII.—*On the Productive Powers of Soils in Relation to the Loss of Plant-food by Drainage.*

By Augustus Voelcker, Ph.D., F.R.S.

(A Lecture delivered before the Chemical Society, May 4th, 1871.)

No person, however slightly he may be acquainted with agricultural chemistry, can fail to recognize the intimate connection which exists between the productive powers of soils and their composition.

The various mineral matters which compose the ash of every description of agricultural produce are as essential to the very existence of plants as oxygen is to the life of animals. These inorganic or ash constituents of plants can only be furnished by the soil upon which they are grown, or by the manure which is purposely put upon the land with the view of supplying any deficiency of plant-food: hence the absence or deficiency in the soil of lime, or potash, or phosphoric acid, or any other essential ash-constituent of plants, renders the land either barren or more or less unproductive. The fertility of land unquestionably depends in a great measure upon the nature and the amount of the stores of mineral plant-food in the soil.

To a person imperfectly acquainted with the teachings of modern agricultural science, and the experience of those who are actually and intelligently engaged in the cultivation of the soil, nothing appears more simple than to recognize the cause or causes of barrenness or comparative unproductiveness of our fields, and to apply the appropriate remedies.

According to the superficial views of a certain class of amateur farmers and chemists, all that requires to be done in order to ascertain why certain soils are almost barren, and others not as productive as it is desirable they should be, is to determine by analysis in what essential plant-constituents they are deficient. Having ascertained this, the remedy in their view, is equally simple. Add to the land, they say those constituents which the plant requires, and which the analysis has shown to be deficient in the land, and the effect will be a luxuriant development of the crops which are intended to be raised upon it.

The amelioration of sterile soils or the restoration of the fertility of land, impaired by constant cropping and bad farming is, however, not quite so simple a matter as it may appear to some people; for, apart from the difficulty of determining with precision the exact composition of soils, and the impossibility of ascertaining by analysis the relative state of

fertility of different fields, a number of conditions have to be considered in addition to the chemical composition of a soil, before we can get an intelligent idea of its agricultural capability.

Allow me, by way of illustration, to direct your attention to a few facts, which it is hoped will show the futility of the endeavour to solve by a mere soil-analysis, the important practical questions, how the fertility of the land is to be maintained or increased.

1. In the first place I would observe that there are many apparently similar soils, that is to say, soils in which the analysis shows like quantities of the same constituents, such as potash, soda, lime, phosphoric, sulphuric acid, &c., and which, notwithstanding, differ widely in their productive powers. This fact plainly shows that soil-analyses, as usually performed by chemists, do not afford in all cases, a sufficient guide for estimating the agricultural capabilities of different soils, or for pointing out the kind of manure which is particularly well adapted for the special crop which we wish to raise.

Even a detailed analysis of a soil gives only the proportions of the different soil-constituents, but generally without reference to the states of combination in which they exist in the soil; and it is altogether silent on the property possessed by all cultivated soils in a higher or lower degree of effecting striking and important changes in the manuring matters which are placed upon the land.

2. Soil-analyses throw no light whatever on the physical or mechanical condition, which affects greatly the fertility of land.

Great stress is laid by Liebig, as it is, indeed, by all good farmers, on the mechanical condition of the land. In dwelling upon the benefits resulting from ploughing, subsoiling, harrowing, and similar means of improving the permeability and general texture of soils, Liebig directs special attention to the physical state of combination, as he calls it, in which mineral plant-food must exist in the surface soil, in order that it may be of service to the growing plant.

Whatever may be the precise meaning of the term, physical state of combination, or whether we assume that mineral food must be presented to plants in solution, or in some other mysterious form, variously represented in Liebig's Law of Husbandry, mineral food certainly cannot be of any service to plants, except it be present in the surface soil in an available form. The word available, perhaps, conveys as correct a meaning as the more novel and less graphic expression physical state of combination.

In such an available combination, the mineral plant-food cannot exist in the surface soil in badly drained land, through which water cannot freely percolate. Thus a soil may contain abundance of potash or phosphoric acid, and all the other food-constituents of plants, and yet be unproductive, simply because it has no natural drainage, or because

it is so stiff or sodden, that the roots of plants cannot penetrate into the soil a sufficient depth in order to grow luxuriantly.

3. Again, a soil analysis may present on paper a very satisfactory aspect, and yet the field from which the analysed soil was taken, may grow but poor crops, for the simple reason that there is no depth of soil to sustain the crop in a growing condition.

4. The productiveness of land is further influenced by the character of the subsoil and its position in relation to the surface-soil; and on these points a soil-analysis conveys no information. Thus, an impervious tile or brick clay subsoil forming a stratum of some 6 to 10 feet, and reaching the surface to within 3 or 4 inches, renders the same soil far less productive than it is in another part of the same field, where the stiff clay subsoil is covered by a greater depth of surface soil.

Supposing the land to be perfectly uniform in composition, and to differ in various parts of the field in no respect, except in the position or the nearness of the subsoil to the surface-soil, and assuming two analyses could be made so perfectly as to yield identical results, two samples of soil, one taken from a part of the field where the stiff clay bed reaches the surface within 4 inches, and another from a part of the field where the same subsoil lies at a depth of 2 feet, would yield precisely the same analytical results, and yet the produce on the two portions of the same field would be very different.

5. The aspect of a field, the prevailing wind, amount of rain, distribution of the rain-fall in the year, and similar purely meteorological conditions, greatly affect the productive powers of land; and on these matters for obvious reasons, the chemical analysis of a soil gives no information.

It is evident, therefore, that on many important points on which information is necessary before a just estimate can be formed of the probable state of the fertility of a field, no light whatever can be thrown by a soil-analysis.

It must not be concluded, however, that because a soil-analysis cannot solve all questions relating to inquiries into the agricultural capabilities of soils, and a rational system of manuring or the proper rotation of crops, it is altogether useless to go to the trouble of analysing soils.

The labour of analysing a soil may be thrown away in some cases, whilst in others the analysis may give us useful information which may be turned to practical account.

Allow me to give a few illustrations showing the utility of a soil-analysis.

1. Many soils, it is well known, are greatly benefited by the application of lime or marl, whilst others are not materially improved

by these means. Now, we can ascertain readily enough by analysis whether a soil is deficient in lime or not, and a farmer may at once determine whether he should go to the expense of liming or marling his land, or not.

2. Experience has shown that potash-salts, which are now imported from the mines at Stassfurt, Leopoldshall, and other places in the North of Germany, at a reasonable cost, may be applied with great advantage to some soils, whilst on others their fertilising effects are scarcely perceptible. A special manure like potash-salts, I need hardly observe, can produce little or no effect upon soils, which like many good agricultural clays abound in available potash. On the other hand, there are soils in which potash does not occur in large proportions, and on such soils the removal of potash in the produce leads to the exhaustion of an element which is beneficially restored to the land in potash-salts.

Sandy soils, generally speaking, are poor in potash, but there are also certain clays more or less resembling porcelain clay, in which the percentage of potash is but very small. On clay-land, resembling in composition porcelain or fire-clay, potash-salts have a good effect, because these clays are naturally deficient in potash.

The determination of potash alone affords us a rapid means of ascertaining whether potash-salts are likely to be of practical utility to the farmer on a particular field.

3. Again we can ascertain, by the determination of potash in clay, whether it is benefited by burning or not.

Burnt clay is an excellent fertiliser if the process of burning is carefully managed and the clay in its natural state contains undecomposed silicates of potash, but the expenses of clay-burning are almost altogether thrown away if the clay is naturally poor in alkaline silicates.

My investigations into the causes of the efficacy of burnt clay as a manure, the details of which will be found in vol. xviii., part II., 1858, of the Journal of the Royal Agricultural Society, have shown me that the main cause of the efficacy of burnt clay as a manure is the potash which is liberated by burning clays containing silicates of potash and carbonate of lime, and rendered available for the use of plants. Consequently no advantage results from burning clays which do not contain an appreciable amount of silicates or double silicates of potash.

4. Peaty soils, or alluvial soils recently reclaimed from the sea, are occasionally completely barren. Their sterility is due in most cases to the presence of sulphate of iron and of finely divided iron-pyrites. Even so small a proportion as $\frac{1}{4}$ per cent. of sulphate of iron renders a soil completely barren.

I may here quote an analysis, which I made a good many years ago,

of a soil from land newly reclaimed from the Haarlem Lake, in Holland. This soil contained 100 parts:—

	Dried at 212° F.
*Organic matter and water of combination	14·71
Oxides of Iron and alumina	9·27
Ferrous sulphate (green vitriol)	·74
Bisulphide of iron (iron pyrites)	·71
Sulphuric acid united with oxide of iron as basic sulphate of iron	1·08
Sulphate of lime	1·72
Magnesia	·73
Phosphoric acid	·27
Potash	·53
Soda	·32
Chloride of sodium	·09
Insoluble siliceous matter (clay)	69·83
	100·00
*Containing nitrogen	·52
Equal to ammonia	·62

This soil abounds in all the mineral elements which enter into the composition of the ashes of plants, and is especially rich in phosphoric acid; it moreover contains a considerable proportion of organic matter capable of yielding on decomposition rather more than $\frac{1}{2}$ per cent. of ammonia, but unfortunately it is impregnated with sulphate of iron, which neutralises all its useful properties, rendering it unproductive.

5. We can ascertain by analysis whether a soil contains an excessive proportion of one or more matters otherwise useful to vegetation. Thus, occasionally, soils contain nitrate of potash or chloride of sodium in proportions which prevent plants either growing at all or only languidly.

As regards soluble saline matters, I may observe that all soils which contain readily soluble salts, such as chloride of sodium, in quantities admitting of precise determination are more or less unproductive, although the salt may be a most effective fertiliser when it is applied in the state of a very weak solution. Thus I find that a soil which contains only $\frac{1}{10}$ per cent. of chloride of sodium hardly grows any crop. In such an unproductive condition land is found which has been inundated by the sea, although it contains scarcely $\frac{1}{10}$ of a per cent. of chloride of sodium.

This proportion may appear extremely small; but, as a matter of fact, $\frac{1}{10}$ of any substance added to a soil amounts to a very much larger quantity than can be safely applied to the land. A little con-

sideration will put this into a clear light. An English acre of soil, 3 inches deep, weighs on an average from 1,000,000 to 1,220,000 lbs., or, in round numbers, 6 inches of soil weigh about 1,000 tons per acre. Consequently, 1 ton of salt incorporated with only 6 inches of soil amounts to only $\frac{1}{10}$ of a per cent. of the weight of the soil. Now every farmer knows perfectly well that a dressing of 1 ton of salt per acre would render his lands sterile for years to come, and he therefore seldom applies more than 2 to 3 cwt. of salt per acre to his land.

These are a few examples, showing that the chemical examination of soils is not without its uses, and the observation just made with reference to the injury caused to growing crops by comparatively small quantities, of very soluble salts, leads me to notice in the next place the remarkably powerful fertilising effects which small quantities of nitrate of soda, or of sulphate of ammonia, or equally soluble nitrates and ammonia compounds, are capable of producing upon vegetation. As little as half a hundred weight of nitrate of soda applied to an acre of grass land, or to wheat or barley, and thoroughly washed into the soil by a good shower of rain, produces a most marked effect, visible in the darker green colour, and greater luxuriance of the herbage in comparison with the colour of these crops not manured with this small quantity of nitrate of soda.

Messrs. Lawes and Gilbert, in their classical field experiments on the continuous growth of wheat on the same land, find that 100 lbs. of ammonia applied to the land in the shape of sulphate or chloride of ammonium, or a mixture of both, raises the average produce in wheat grain 20 bushels, with a corresponding increase of wheat straw; or the natural produce of the unmanured land, amounting to 15 bushels per acre, is at once raised to 35 bushels of corn by the application of 100 lbs. of ammonia per acre. Assuming 6 inches of soil to weigh 2,000,000 lbs. per acre, the addition of 100 lbs. of ammonia will represent only ·0033 of a per cent., but even this small addition of an ammoniacal salt to the land, provided it contains the requisite amount of mineral plant food, is sufficient to produce this marvellous increase.

Or, taking another example, which illustrates the same point, 3 cwts. of superphosphate of lime, of good quality, added to 6 inches of soil hardly adds $\frac{1}{60000}$ of a per cent. of phosphoric acid to the land, and yet such an application has the effect of increasing the turnip crop in favourable seasons from 6 to 10 tons per acre.

I need hardly say that so small an amount of phosphoric acid cannot be accurately determined, and yet there is a great deal of difference in the turnip-producing qualities of land manured with 3 cwts. of a good superphosphate and land left unmanured.

The two last-mentioned facts clearly show how utterly futile it is to determine the relative state of productiveness of different soils by

analysis. They likewise afford grounds for opposing the views of those who advocate, in a system of rational farming, to keep up a debtor and creditor account as regards the constituents which are removed from the soil in the crop grown upon it, and the quantities of fertilising matters which should be returned to it in the shape of manure. If time permitted, it might be readily shown in detail that the fertility of the land cannot be maintained in a desirable condition, much less be increased, if the farmer applies merely the same amount of fertilising constituents which he removes from the land in the crops he grows. In fact, a farmer like some of my chemical experimental agricultural friends, would soon come to wreck and ruin were he to keep up a chemical balance account of the resources and outgoings of a farm, which has been suggested by no mean authority should be done by every farmer.

Unless I am much mistaken, I am inclined to think that at least three to five times as much of all the more important fertilising matters has to be put upon the land as is removed from it in the crops, or that such an excess of fertilising matters must be rendered available by good cultivation if the soil contains naturally a practicable inexhaustible store of mineral food, if a man wishes to make a living by farming. Taking for guide the experience of good farmers, I do not hesitate to say that, as a rule, infinitely more available fertilising matter is put upon the land in practice by all who farm for profit, and not merely for amusement's sake, than is removed in the crops grown upon the land. Generally speaking, the man who grows heavy crops, or in other words, who takes much out of the land, is precisely the man who restores greatly more of the elements of fertility than he removes in the produce. High farming has been branded by some as a system of robbery, but a more inappropriate name it strikes me could hardly be applied to a system of farming, which I understand to consist in the skill of the farmer to produce profitably large crops without injury to the land; and as just now observed, this cannot be done profitably unless much more nitrogen, phosphoric acid, &c., is returned to the land than is removed in the crops.

Experience, moreover, has shown that, although the incorporation with the soil of large quantities of mineral and organic fertilising matters raises its productive powers for a season or two, the land rapidly returns to its natural state of fertility if it be left for a few seasons without a constant supply of organic or mineral food, or both as may be required.

It is also well known to all acquainted with farming operations, that whilst some plant-constituents, when added to the land, hardly produce any effect upon the produce, others have a marvellous effect.

Thus purely mineral manures, that is to say, manures composed of

the ash-constituents of plants, produce an effect upon the crops usually grown in the course of a rotation, only in exceptional cases, and as a rule are more or less ineffective when applied to most soils in the ordinary course of farming, whilst comparatively speaking, small quantities of ammoniacal salts, as in Messrs. Lawes and Gilbert's experiments—experiments confirmed on a large scale by the experience of all good farmers—produce a very large increase of wheat, barley, and other cereal crops.

It is worthy of notice that in Lawes and Gilbert's experiments, the increased yield of wheat could only be maintained as long as the supply of ammonia salts was kept up from year to year. Left a single year without the addition of the ammoniacal salts, the land at once ceased to give the customary increase in corn, and the produce sank to an amount differing but little from that upon which wheat was grown for years in succession without any manure.

Lawes and Gilbert's experiments on the continuous growth of wheat are peculiarly interesting in relation to a subject with which I have been actively occupied during the last three years, namely, the examination of land-drainage waters.

Messrs. Lawes and Gilbert, throughout a long series of experiments on the growth of wheat, invariably experienced a great loss of nitrogen, no matter whether ammoniacal salts or nitrates, or nitrogenous organic matters, were applied to the wheat crop, and a similar loss in nitrogen was experienced when barley or meadow hay was grown. The following table, kindly furnished to me by Messrs. Lawes and Gilbert, shows the amount of nitrogen in the increased produce for 100 in the manure:—

INCREASED Nitrogen in produce for 100 supplied in manure.

Crops.	Number of years.	Increased nitrogen in produce for 100 in manure.
Wheat.....	6	43·0
Barley.....	6	42·5
Meadow hay	7	44·8

It appears from this table that the amount of nitrogen supplied in the manure was very much greater than that recovered in the increased produce. Searching for the loss, Lawes and Gilbert naturally directed their attention to the investigation of the amount of nitrogen which probably accumulated in the land considerably under a liberal nitrogenous treatment of manuring.

By a series of careful determinations, Lawes and Gilbert ascertained

the relative proportions of nitrogen in the soil at various depths and under different conditions of manuring. Although by the use of farmyard manure and other nitrogenous fertilising matters, the percentage of nitrogen in the soil increased to some extent, yet the nitrogen thus accumulated in the land, added to that in the increased produce, left a considerable deficiency which could not be accounted for in a rational manner, and on the bases of well-ascertained facts.

This subject was prominently brought forward in 1866, at the Nottingham Meeting of the British Association, in a paper by Messrs. Lawes and Gilbert, "On the Accumulation of the Nitrogen of Manure in the Soil." In the report on this paper, it is stated, amongst other particulars, that the authors found, "that although a considerable amount of the nitrogen supplied in manure, which had not been recovered as increase of crop, was shown to remain in the soil, still a larger amount was as yet unaccounted for. Initiative results indicated that some existed as nitric acid in the soil, but it was believed that the amount so existing would prove to be but small. In fact, it was concluded that a considerably larger proportion would remain entirely unaccounted for within the soil to the depth under examination than was there traceable, and the probability was, that at any rate some of this had passed off into the drains, and some into the lower strata of the soil."

It having appeared to me likely that the loss of nitrogen by drainage first pointed out by Messrs. Lawes and Gilbert, would be found to be considerable, I resolved to make a thorough examination of land-drainage waters. Mr. Lawes not only complied with my request to provide me with drainage water from unmanured and from highly-manured fields, but he supplied me with a series of drainage-waters which I could not have obtained anywhere else under equally favourable conditions.

Mr. Lawes kindly directed holes to be dug in his experimental wheat-field at the end of each drain, passing right through the middle of each experimental plot, and thus afforded me the opportunity of examining the drainage, which was collected from time to time, and sent to me by my friend Dr. Gilbert.

Before stating the results of analyses, which occupied me more or less during the last three years, it may be desirable briefly to mention with what manures and what quantities the wheat was grown on the different plots from which I received the drainage water for examination. Each plot under experiment occupies the space of two-thirds of an acre.

Plots No. 2 and No. 16 were left unmanured.

Plot No. 3 was continuously manured from year to year with farmyard manure.

On Plots 5, 6, 7, 8, and 9 the same minerals were used. No. 5 not receiving ammonia, and 6, 7, and 8 varying quantities of ammonia salts, and No. 9 nitrate of soda instead of ammonia salts. On Plots 10, 11, 12, 13, and 14, and 7, the same amount of ammonia salts (400 lbs. equalling 82 lbs. of nitrogen) were used with varying mineral associations.

Further particulars as regards the manures used will be seen on throwing a glance at the tabulated statement of the mean results of my drainage-water analyses.

As regards the methods employed in the analyses, I may observe that the usual approved plans of determining lime, magnesia, and other ordinary mineral matters, were followed. The ammonia was determined in the distillate from a pint of water and the nitric acid by Pugh's method. For the determination of phosphoric acid half a gallon of the drainage water was evaporated to dryness, the residue taken up with nitric acid, and in the nitric acid solution the phosphoric acid thrown down with molybdic acid, and the percentage of phosphoric acid was finally ascertained as ammonia phosphate of magnesia.

Drainage-waters were collected :—

1866, December	6,	at a full flow of the drains	
1867, May	21,	,,	,,
1868, January	13,	,,	,,
1868, April	21,	,,	,,
1869, Dec.	29,	at an enormous flow of the drains.	

The following large table shows the mean composition of drainage-water from plots differently manured. Broadbalk Field, Rothamsted; wheat every year, commencing 1844.

At the bottom of the table I have placed the details of nitric acid determinations and the total solid matter per gallon.

COMPOSITION OF DRAINAGE-WATER FROM

Broadbalk Field, Rothamsted; Wheat

Manures stated in quantities per acre; Constituents

	Farmyard manure every year.	Unmanured every year.	Superphosphate and sulphates of potash, soda, and magnesia.				
			Without ammonia salts.	And 200 lbs. ammonia salts. (41 lbs. N.)	And 400 lbs. ammonia salts. (82 lbs. N.)	And 600 lbs. ammonia salts. (123 lbs. N.)	And 550 lbs. nitrate of soda. (82 lbs. N.)
	Plot 2.	Plots 3 & 4.	Plot 5.	Plot 6.	Plot 7.	Plot 8.	Plot 9.
Mean							
Peroxide of iron	0·18	0 40	0·31	0·19	0·57	0·19	0·36
Lime	10·32	6·87	8·70	10·07	12·70	13 81	8·27
Magnesia	0·34	0·36	0·45	0·55	0 58	0·62	0·41
Potash	0·38	0·12	0·38	0·31	0·20	0·19	0·29
Soda	0·96	0·42	0·82	0·75	0·76	0·74	3 93
Chlorine	1·45	0·75	0·78	1·45	1·83	2·76	0·84
Sulphuric acid	7·43	1·73	4·64	5·13	6·31	6 28	2 87
Phosphoric acid	—	0·044	0·064	0·108	0·064	0 012	—
Soluble silica	2·50	0·76	1·08	1·73	1·19	1·46	0·74
Ammonia	0·014	0·010	0·011	0·017	0·006	0·023	0 020
Nitric acid	4·34	1·05	1·37	2·30	3·78	4·55	0 96
Loss by ignition, carbonic acid, and difference	5·42	4·74	4·21	5·92	6·48	7·75	6·98
Total solid at 260° F.	33·33	17·25	22·82	28·53	34 47	38·39	29·67
Detail—							
1866, December 6	5·28	1·75	2·37	3·59	5·86	6 93	1·91
1867, May 21	—	0·14	0·16	0·24	0·21	0·74	2·12
1868, January 13	3·39	1·80	2 50	4·60	7·59	8·38	3·23
1868, April 21	—	0·23	0·37	0·51	1·21	1·63	15·74
1868, December 29	—	1·35	1·43	2·57	4·03	5·06	1·78
Means	4·34	1·05	1·37	2·30	3·78	4·55	4·96
Detail—Total							
1866, December 6	37·75	21·15	26 85	37 10	48·65	48·75	29·40
1867, May 21	—	16·65	20·25	23·15	25 10	31·35	27·01
1868, January 13	28·90	18 11	28 35	36·75	44·55	50·45	24·85
1868, April 21	—	14·15	18·85	22·80	23·65	26·80	47·85
1868, December 29	—	16·20	19·80	22·85	30·40	34·60	19·25
Means	33·33	17·25	22·82	28·53	34·47	38·39	29·67

PLOTS DIFFERENTLY MANURED.

every year, commencing 1844.

in Drainage Water in grains per gallon.

400 lbs. ammonia salts (82 lbs. N).					Bone-ash, HCl, and sulphate of ammonia.	Mineral manure and 800 lbs. ammonia salts, 1852—1864 Unmanured 1865, and since.	Means.	
Without mineral manure.	With superphosphate of lime.	With superphosphate and sulphate of soda.	With superphosphate and sulphate of potash.	With superphosphate and sulphate of magnesia.				
Plot 10.	Plot 11.	Plot 12.	Plot 13.	Plot 14.	Plot 15.	Plot 16.		

Results.

0·28	0·24	0·25	0·26	0·26	0·24	0·21	0·28	Peroxide of iron
10·79	11·59	13·41	14·10	15·87	14·08	8·20	11·34	Lime
0·52	0·51	0·46	0·65	0·81	0·55	0·37	0·51	Magnesia
0·13	0·07	0·19	0·23	0·08	0·37	0·17	0·22	Potash
0·50	0·46	1·72	0·43	3·39	1·00	0·36	0·95	Soda
2·24	2·21	2·16	2·56	2·76	1·72	0·80	1·74	Chlorine
3·11	3·80	6·77	6·08	6·98	8·67	1·53	5·10	Sulphuric acid
0·102	0·116	0·088	0·076	0·071	0·108	0·064	0·076	Phosphoric acid
0·96	0·79	1·25	1·98	0·98	1·55	1·19	1·30	Soluble silica
0·007	0·015	0·025	0·013	0·008	0·009	0·008	0·013	Ammonia
3·75	4·14	4·08	4·71	5·18	6·54	1·89	3·76	Nitric acid
6·09	5·87	6·76	7·01	8·51	6·13	5·28	6·21	Loss by ignition, carbonic acid, and difference
28·48	29·81	37·16	38·10	41·90	40·97	20·07	31·50	Total solid at 260° F.

Nitric Acid.

—	6·11	7·06	7·55	8·07	—	2·43	4·91	1866, December 6
0·11	0·14	0·29	0·25	0·32	—	0·28	0·42	1867, May 21
6·84	7·77	8·13	9·46	10·19	12·55	3·65	6·43	1868, January 13
2·74	2·06	0·47	1·52	1·82	2·05	1·59	2·46	1868, April 21
5·29	4·63	4·44	4·78	5·52	5·01	1·49	3·64	1868, December 29
3·75	4·14	4·08	4·71	5·18	6·54	1·89	3·76	Means

Solid Matter.

36·85	35·55	49·35	51·95	56·01	—	23·23	38·66	1866, December 6
21·91	26·90	29·95	32·05	32·60	—	21·41	25·70	1867, May 21
34·85	38·05	46·10	47·05	53·41	57·55	20·76	37·84	1868, January 13
22·65	20·90	26·91	27·75	29·65	27·91	18·67	25·27	1868, April 21
26·15	27·65	33·50	31·70	37·85	37·45	16·30	27·21	1868, December 29
28·48	29·81	37·16	38·10	41·90	40·97	20·07	31·50	Means

The following are some of the more interesting and important results which the investigation has brought to light:—

First Series, December 6, 1866.—The quantities of nitric acid varied much in the drainage-water from the different plots. The total amount of solid matter varied in the different fields from 21·15 to 56·01 grs. in the gallon.

Farmyard-manure contains no nitrates, but the drainage-water of the field manured with farmyard-manure contained 5·28 grs. of nitric acid.

In the adjoining unmanured plot the drainage-water, collected on the same day, contained only 1¾ grs. of nitric acid, and the second unmanured plot 2·43 grs. of nitric acid.

It is worthy of observation that the drainage-water of the land to which nitrate of soda was applied in spring, contained no more nitric acid than the water from the unmanured plot, showing that soils have not the power of retaining nitrates.

Although some of the experimental plots were dressed with considerable quantities of ammoniacal salts, the drainage-waters contained only minute quantities of ammonia.

Practically the ammoniacal salts were gradually and completely oxidized and converted into nitrates, which passed away by degrees as nitrates in the drainage-water.

It will be seen that the amount of lime in the drainage water from the plots to which ammoniacal salts were applied was very much larger than in the water from the parts of the field which were left unmanured. The lime passed away chiefly as nitrate of lime.

All the drainage waters from the plots to which chlorides or sulphates were applied contained considerably more chlorine and sulphuric acid than the drainage from the plots to which no chlorides or sulphates were applied. The soil does not possess the power of absorbing the acid elements of these salts.

Second Series, collected May 20th, 1867.—In this series I determined, in addition to other constituents, the amount of potash and soda in the drainage-waters.

1. As regards the total amount of solid matter, the waters contained less solid matter in June than in December of the preceding year.

2. With the exceptions of plot 9, where nitrate of soda was used, the drainage water contained only minute quantities of nitric acid.

3. The amount of nitric acid in the water from plot 9 was about the same as from the same plot in December, and the total amount of solid matter in the water from plot 9 was nearly the same in June as in December.

4. It would appear, therefore, that during the active growth of wheat, either the nitric acid is consumed by the plant or the ammoniacal salts applied to the land are not transformed at that period into nitrates.

5. The drainage-waters contained very little potash, showing that soils have the power of retaining potash.

6. On the other hand, the proportions of soda in the drainage-water was larger on the plots to which nitrate and sulphate of soda were applied, showing a marked difference in the selective powers of soils for potash and soda.

7. The differences in the proportion of lime and sulphuric acid in the different drainage-waters are great, and, as a rule, the greater the proportion of lime in the drainage, the more sulphuric acid occurred in it at the same time.

It thus appears that sulphate of ammonia, in passing through the soil is decomposed, and whilst the acid passes away in the drainage in combination with lime, the ammonia is retained in the soil.

All the waters contained only traces of ammonia, which was not determined quantitatively.

In three instances the amount of phosphoric acid was determined. The quantity of phosphoric acid in drainage-water is but small, and therefore not less than half a gallon was evaporated, the phosphoric acid being determined in the residue by molybdate of ammonia, and finally weighed as magnesia phosphate.

Third Series, January 13th, 1868.—1. The total amount of fixed matter varied in the different parts of the field between 18·11 grs. and 57·55 grs.

2. The water from all the plots contained only traces of ammonia.

3. All, even the unmanured portions, contained appreciable quantities of nitric acid.

4. The amount of nitric acid was greater in the drainage from the plots to which ammoniacal salts were applied in large proportions, than in the drainage from the plots on which they were used more sparingly.

5. The amount of nitric acid was smaller in the drainage from the plots to which nitrate of soda was applied in the preceding spring than from the plots to which ammoniacal salts were applied, showing that the greater part of nitrates was removed by the rainfall during the autumn.

6. The amount of lime removed in the drainage waters corresponded with the amount of nitric acid in the water. With an increasing proportion of lime in the water, that of nitric acid increased.

7. More magnesia was found in the drainage-water from the plots to which sulphate of magnesia was applied than where no sulphate of magnesia was used.

8. All the waters contained but little potash, showing that the soil has the power of retaining potash.

9. On the other hand, soda was found more abundantly in the drainage water from the plot upon which nitrate and sulphate of soda were used.

10. The amount of sulphuric acid was much smaller in the drainage water from the land to which no sulphates were applied than from the field manured with sulphates.

11. The drainage waters which were examined for phosphoric acid contained appreciable quantities of this acid.

Fourth Series, April 21*st*, 1868.—In the drainage from most of the plots, the total amount of solid matter varied much less than in the drainage water collected in the preceding series. The total amount of solid matter varied from 14·15 grs. to 29·65 grs. per gallon, with the exception of the nitrate of soda plot, in the drainage of which the exceptionally high amount of 57·85 grs. of solid matter occurred.

2. All the waters contained merely traces of ammonia, although on many of the plots large quantities of ammonia-salts were used.

3. The drainage waters contained comparatively but little nitric acid, except the drainage from the plot on which nitrate of soda was used.

4. In the drainage from the nitrate of soda plot both the amount of nitric acid and soda was large, showing that a great deal of nitrate of soda was washed away and passed into the drainage.

5. Practically no potash was removed.

6. Sulphate of soda passed through the soil, and to some extent also sulphate of magnesia.

7. All the waters from the plots to which superphosphate or salt was applied contained more phosphoric acid and more chlorine than the unmanured plots.

8. The amount of soluble silica in some of the waters is remarkably great.

9. The 2nd unmanured plot, which, however, was manured in previous years, showed still in the drainage-water a larger amount of soluble fertilizing matters than plot 3.

Fifth Series, Dec. 29, 1868.—1. The total amount of solid matters varied from 16·20 grs. to 37·85 grs. per gallon.

2. All the waters from the different plots contained nitric acid.

3. The drainage from the unmanured plots contained scarcely less nitric acid than the drainage from the plot upon which nitrate of soda was used in the preceding spring.

4. On the other hand, more nitric acid was found in the water from the plots to which the larger quantities of ammonia salts were applied than in the drainage from the plots on which smaller quantities were used.

5. Potash, soda, lime and magnesia, and sulphuric acid as before.

DRAINAGE-WATER FROM PLOTS DIFFERENTLY MANURED.

Broadbalk Field, Rothamsted; Wheat every year, commencing 1844.

Nitrogen as Nitrates and Nitrites, per 100,000 *parts of Water.*

	Farm-yard manure every year.	Unmanured every year.	Superphosphate and sulphates of potash, soda, and magnesia.					400 lbs. ammonia salts (82 lbs. N).					Mineral manure and 800 lbs. ammonia salts 1852—1864. Unmanured 1865—1871.	Means.
			Without ammonia salts.	And 200 lbs. ammonia salts (41 lbs. N).	And 400 lbs. ammonia salts (82 lbs. N).	And 600 lbs. ammonia salts (123 lbs. N).	And 550 lbs. nitrate soda (82 lbs. N).	Without mineral manure.	With superphosphate of lime.	With superphosphate and sulphate of soda.	With superphosphate and sulphate of potash.	With superphosphate and sulphate of magnesia.		
	Plot 2.	Plots 3, 4.	Plot 5.	Plot 6.	Plot 7.	Plot 8.	Plot 9.	Plot 10.	Plot 11.	Plot 12.	Plot 13.	Plot 14.	Plot 16.	
1866, Dec. 6, full flow	1·956	0·648	0·878	1·330	2·170	2·567	0·707	—	2·263	2·615	2·796	2·989	0·900	1·818
1867, May 21, full flow....	—	0·052	0·059	0·089	0·078	0·274	0·785	0·041	0·052	0·107	0·093	0·119	0·104	0·154
1868, Jan. 13, full flow....	1·256	0·667	0·926	1·704	2·811	3·104	1·196	2·533	2·878	3·011	3·504	3·774	0·659	2·156
1868, April 21, full flow ..	—	0·085	0·137	0·189	0·448	0·578	5·830	1·015	0·763	0·174	0·563	0·674	0·589	0·920
1868, Dec. 29, enormous flow	—	0·500	0·530	0·952	1·493	1·874	0·659	1·959	1·715	1·644	1·770	2·044	0·552	1·308
Means	1·606	0·390	0·506	0·853	1·400	1·679	1·835	1·387	1·534	1·510	1·745	1·920	0·561	1·302

SUMMARY.

	Plot 2. Farmyard manure.	Plots 3, 4, 5, and 16. No N. in manure.	Plot 6. 41 lbs. N. as ammonia.	Plots 7, 10, 11, 12, 13, and 14. 82 lbs. N. as ammonia.	Plot 9. 82 lbs. N. as nitric acid.	Plot 8. 123 lbs. N. as ammonia.
1866, Dec. 6, full flow	1·956	0·809	1·330	2·567	0·707	2·567
1867, May 21, full flow....	—	0·072	0·089	0·082	0·785	0·274
1868, Jan. 13, full flow....	1·256	0·751	1·704	3·085	3·196	3·104
1868, April 21, full flow ..	—	0·270	0·189	0·606	5·830	0·578
1868, Dec. 29, enormous flow	—	0·527	0·952	1·771	0·659	1·874
Means	1·606	0·486	0·853	1·622	1·835	1·679

In order that my nitric acid determinations may be compared with others that have been obtained or may be obtained in similar experiments, I append a table in which the amount of nitrogen as nitrates and nitrites has been calculated per 100,000 parts of water.

With regard to the actual loss which our cultivated, and it may be highly manured fields sustain by drainage, I would observe that we possess no trustworthy data from which an average estimate can be made of the amount of rain which is disposed of by evaporation from the surface, and by passage into the drains, and for this reason I will not touch on this occasion on the researches of Maurice of Geneva, Gasparin at Orange, Dalton in Manchester, Dickinson in Hertfordshire, and more recently by Mr. Risler of Geneva, or Messrs. Lawes and Gilbert, who have endeavoured to determine the relation of surface evaporation and the loss of water by drainage.

The loss of water, and with it of fertilising matter, must naturally vary a great deal in different soils, and according to the distribution of the rain in the year, and the quantity which falls at one period. In the absence of satisfactory evidence from which may be deduced the probable amount of water which passed through the drains of the experimental wheat field at Rothamsted, it is impossible to say how much of the nitrogen, which was neither recovered in the produce nor accumulated in the soil is due to drainage. My own impression is, that probably the whole of the experienced loss may be satisfactorily accounted for, when the actual quantities of water which passes through the soil shall have been carefully weighed and the composition of the whole drainage been ascertained. At all events, whether nitrogen is applied to the soil in the shape of nitrogenous organic matter, or in the shape of ammonia salts or of nitrates, my experiments clearly show that a large proportion of the nitrogen supplied in the manure, is carried off by the drains chiefly in the form of nitrates.

Nitrate of soda more especially appears to be rapidly removed by the rain that falls upon the land into the subsoil or into the drains, for it is well known that soils do not possess the power of absorbing and retaining nitrates for any length of time. It follows further from my experiments that although all soils possess the power of absorbing ammonia in smaller or larger quantities, yet the ammonia thus absorbed is rapidly oxidised in porous soils, and much of the nitrogen supplied to the land in the shape of ammonia salts passes off into the drains as nitrates and is lost.

Nitrogenous organic matters, when applied to the land in the shape of manures, suffer decomposition, and are gradually resolved at first into ammonia compounds, which are retained by the soil for a limited time, and finally these compounds are oxidized into nitrates, which make their appearance just at the time when vegetation makes a fresh

start in spring, and which must then be consumed by the plant, or they will be lost, and be of no use to the succeeding crop. Nitrate of soda which is largely used as a top-dressing for cereal crops, thus, should be applied late in spring, the best time in average seasons being probably the middle of March, whilst sulphate of ammonia and other ammoniacal manures may be applied to the land with less risk of being washed away in February, or the beginning of March. Farmyard manure, fresh from the stable or cattle sheds, on the other hand, experience has shown, is best applied in autumn, and if it be the case that nitric acid is, *par excellence*, the combination from which plants derive their organic nitrogen, we can readily understand why fresh excrementitious matters should be applied to the land in autumn. At all times of the year, but more especially during the most active period of growth, nitrates are invariably found in considerable quantities in the watery liquid which circulates in the land, whereas ammonia salts are never found in any appreciable quantities in that liquid. It may therefore be assumed that it is chiefly, if not solely, from nitrates, that our crops build up their nitrogenous organic constituents.

It will be noticed that the examination of these drainage-waters clearly shows that potash and phosphoric acid, which are certainly the most important mineral constituents of soils and manures, are almost altogether retained in the soil, whilst the less important, because more abundant and widely distributed, mineral matters, such as lime, or magnesia, or sulphuric acid, pass with greater readiness through the land.

The property of soils of modifying the composition of the manures, and of preparing plant-food, which may be assumed to circulate in the watery liquid from which plants derive nourishment, is strikingly illustrated in the analyses of the drainage waters.

It is not necessary to dwell upon the importance of an accurate knowledge of the inherent capacity of different soils to work up, so to speak, the crude fertilising matters into new combinations, and to provide for a constant supply of food, which is neither so soluble as to injure the crop, nor so insoluble as to remain inactive.

The investigation of the exact circumstances under which these properties manifest themselves, has an important bearing on the *rationale* of the rotation of crops and the economy of manures. Such an investigation opens a wide field of research, and if prosecuted in a truly scientific spirit, will be assuredly followed by useful applications.

It must, therefore, ever be the primary object of every student of nature, whether he be more specially occupied with applied science, or with the investigation of more purely theoretical branches of science, to increase our knowledge of scientific facts, and thus to furnish the materials from which principles can be deduced and upon which

rational theories can be built. Perhaps no theory in physical science is absolutely true; nevertheless, if it fulfil the chief purpose of every good theory, that is, the arrangement of existing scientific facts in a comprehensive form, and their preservation as a common inheritance to mankind, and so leads to an extension of our knowledge of material things, no theory, however erroneous subsequent researches may prove it to be, can be called vain.

Discussion.

Dr. Warren De la Rue said that some experiments of his own, made upon a plot of sandy soil, enabled him to corroborate Dr. Voelcker's remarks as to the importance of observing the proper season for applying nitrates and ammonia salts to the land.

Dr. Gilbert fully concurred with Dr. Voelcker as to the inapplicability of soil analyses conducted according to the usual methods, for the settlement of many questions for which they had been recommended on high authority. After fully considering the subject, at the commencement of their own investigations, Mr. Lawes and he had come to the conclusion that synthesis, so to speak, was their best method of analysis. By growing crops year after year on the same land, without manure, and with different constituents of manure, singly or in admixture, they had tested the productiveness and the requirements of the soil much better than any analysis could do. They had always urged that the determination of the main physical and chemical characters, and of certain properties of soils, as to their power of absorption and retention of water, ammonia, and some other matters, was more instructive than what was generally understood as the analysis of the soil. Turning to that part of the Lecture which related to the results of the complete analysis of 70 samples of drainage-water from experimental plots at Rothamsted, Dr. Gilbert felt sure that the Society would feel greatly indebted to Dr. Voelcker for so valuable a contribution to our knowledge of a subject of growing importance in many points of view. He much regretted the absence of Dr. Frankland, who had also analysed drainage-waters from some of the same experimental plots, and from his results had concluded that there was so much mixture of the waters from plot to plot, that the composition of the drainage from any individual plot was not dependent on the manure of that particular plot, but was very much affected by the manuring of the whole field. The fact was that, at Dr. Frankland's own request, some of the waters supplied to him were the first dribblings from the drains succeeding a period of dry weather; and these being, therefore, very concentrated, a comparison of his results as a whole did not show the characteristic differences according to the manure employed, which were very striking

throughout Dr. Voelcker's more extended series of results, all obtained upon samples collected when the drains were running freely. Dr. Voelcker's results clearly showed that phosphoric acid and potash, the soil-constituents of most value, in the sense that they are the most liable to be wanting in available quantity, were, at any rate in certain soils, comparatively very little subject to loss by drainage; and it was further of interest to observe, as bearing upon the view according to which one chief function of ammonia-salts was the solution of certain mineral constituents, that the amount of neither of these substances was increased in the drainage-water with an increased supply of ammonia-salts to the soil. It was, in fact, chiefly the lime, in small amount the magnesia, but largely the sulphuric acid, the chlorine, and the nitric acid, that were increased in the drainage with the increased supply of ammonia-salts, the latter being applied as an equal mixture of the sulphate and muriate of commerce. The point of greatest importance was, however, the loss of nitrogen in the form of nitric acid, which was obviously very much the greater the larger the amount of ammonia-salts applied, especially during the winter months, when there was little or no vegetation. It had been found at Rothamsted that when nitrogenous manures were used for cereal crops or grass, generally less than half of the nitrogen so supplied was recovered in the increase of produce obtained. At one time Mr. Lawes and himself, relying upon the observations of some vegetable physiologists, had supposed that nitrogen, free or combined, was evolved from the leaves of plants during growth; but, partly as the result of direct experiments on vegetation at Rothamsted, and partly for other reasons, they had been led, some years ago, to consider this explanation improbable. Liebig had assumed that the amount unrecovered in the season of application, accumulated in the soil, and that to it, rather than to fresh supplies added, was due the increase of produce obtained in subsequent years. Their own determinations of nitrogen in the soils of the experimental plots did show that there was a considerable accumulation, but field results proved that this residue was very slowly available, if ever completely, to succeeding crops; whilst the amount accumulated was far from sufficient to account for the whole loss. When commenting on this result at the meeting of the British Association in 1866, they had stated it as their conclusion, that drainage would probably account for much, if not all, of the remaining loss; and Dr. Voelcker's results showed that the loss in that way must, at any rate, be very considerable. The difficulty was, however, to determine what proportion of the rainfall, probably on the average, drained away beyond the reach of the roots of the growing crops. Of course the amount must vary much with soil and season. From direct experiments, Dalton concluded that 25 per cent., Maurice that 39 per cent., Gasparin that 20 per cent., Dickinson that 42½ per cent., and Risler that 30 per cent. of the

rainfall of their respective localities passed away by drainage. Experiments were now being made on the subject at Rothamsted; and although they were at present only initiative, it might be stated that, during a period of 8 months, from September 1st, 1870, to the end of April 1871, drainage, equal to about 7 inches of rain, had passed below 40 inches, and an amount, equal to about 4 inches, below 60 inches from the surface.

The important practical bearings of these enquiries would be at once obvious, when it was observed, that several of Dr. Voelcker's results showed as much as 3 parts of nitrogen in the form of nitrates and nitrites per 100,000 parts of drainage, and when it was further stated, that for every inch of rain so carrying with it 1 part of nitrogen per 100,000, there was a loss of about $2\frac{1}{4}$ lbs. of nitrogen of manure per acre. Indeed, one of Dr. Voelcker's results showed 5·83 parts of nitrogen as nitrates and nitrites per 100,000 parts of drainage, after a recent application of a heavy dressing of nitrate of soda; and provided an inch of rain then passed away, this would be equivalent to a loss of about 13 lbs. of nitrogen per acre. The importance of Dr. Voelcker's results in their bearings on agricultural problems was, therefore, very great; but they were also of interest in connection with the question of the influence of the sources of our water-supplies upon the composition and quality of the water.

Dr. Marcet thought that strict analogy exists between animal and vegetable physiology. The soil, like the blood, does not retain those substances it has no need of, but keeps well those necessary for the life of the plant. How they are retained, in what state they exist in the ground, we do not know. Liebig thinks that the soil holds them like charcoal holds certain salts, or some colouring matters. They are not in a state we usually call soluble, for then they would too readily pass from the land; on the other hand, they cannot be insoluble, or else the plant could not avail itself of them. These mineral matters must, therefore exist in a kind of intermediate state. Paying attention to that peculiar property of the soil of retaining the useful constituents and eliminating the unnecessary ones, Dr. Marcet believes nitric acid to belong to the latter class, since it is met with in the drain-waters.

Mr. Warington thought that the analogy drawn by the previous speaker was not quite a correct one; the body was a *living* medium, but the soil was not. As to the supposition that nitric acid is not among those substances which the plant requires, he need merely point to the results obtained by manuring a field with sodium nitrate. Alluding then to Dr. Voelcker's statement, that at all seasons of the year, the drain-waters contain valuable plant-constituents, Mr. Warington regarded this fact as contradictory to the opinion held by men of authority, that immense returns in produce would follow the appli-

cation of sewage-manure by means of irrigation, since this would have to be done during periods when the activity of the vegetation was almost nought. As to the observation that nitrates are not well retained by the soil, Mr. Warington thought that some facts seemed to show the existence of a small power of retention, which had hitherto been overlooked. Pointing to the table (p. 291), which showed that smaller quantities of nitrogen had passed into the drains from the plot manured with sodium salts than from the plot manured with potassium salts, and less again from this than from that receiving magnesium salts, Mr. Warington remarked that this fact could have been predicted from what Professor Way had observed, viz., that the double salt of alumina and ammonia was more easily decomposed by magnesium salts than by salts of potassium or sodium.

Mr. Grantham briefly mentioned that there are now drain-gauges set up on the fields where irrigation experiments are carried on under the direction of the British Association Committee, and he thinks that results bearing upon the question of the evening will be soon obtained.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

On the Unequal Conducting Power of Gases for Heat.

By F. Mohr.*

The following considerations are intended to throw light on the unequal conducting power of gases for heat, discovered by Magnus.

Let the mass of one gas be m, its velocity c, and of another gas M and C respectively, we have, in consequence of the equality of tension: $mc^2 = MC^2$, and, therefore, $c : C = \sqrt{M} : \sqrt{m}$, that is, *at equal pressure the velocities of the atoms or molecules of gases are inversely proportional to the square roots of their specific gravities.* Taking the sp. gr. of hydrogen as our unit, and assuming the velocity of its atoms to be 100, we obtain the following relative velocities of various gases, under like conditions of pressure and temperature:—

Substance.	A Specific gravity.	$\sqrt{A}$	Relative velocity. Hydrogen = 100. $\left(\frac{100}{\sqrt{A}}\right)$
Hydrogen	1	1	100
Air	14·5	3·807	26·3
Ammonia	8·5	2·915	34·3
Carbonic acid.....	22	4·69	21·4

Now the propagation of heat through gases takes place by actual contact as well as by radiation. The particles impinging upon a heated body receive heat and transfer it to other less heated parts. It is clear, therefore, that gases possessing the greatest velocity will produce the greatest number of impacts, and will abstract the greatest amount of heat. Now Magnus has experimentally determined the time necessary for producing a given increment of temperature in a thermometer in different gases, when exposed to a constant source of heat.

The following table gives the results:—

Time necessary to raise the thermometer—

In	From 20°—80° C.	From 20°—90° C.
Hydrogen	1 minute	1·41 minutes.
Air	3·5 ,,	5·23 ,,
Ammonia	3·5 ,,	5·37 ,,
Carbonic acid.....	4·25 ,,	6·37 ,,

* Deut. Chem. Ges. Ber., iv, 85—90.

If now we take the conducting power of hydrogen equal to 100, and calculate those of the other gases by dividing 100 and 141 respectively, by the time necessary to raise the temperature an equal amount, we obtain the following numbers:—

Calculated velocity.

Substance.	From the series 20°—80° C.	From the series 20°—90° C.	From the specific gravity, according to the method of the author.
Hydrogen	$\frac{100}{1} = 100$	$\frac{141}{1 \cdot 41} = 100$	100
Air	$\frac{100}{3 \cdot 5} = 28 \cdot 5$	$\frac{141}{5 \cdot 23} = 26 \cdot 9$	26·72
Ammonia	$\frac{100}{3 \cdot 5} = 28 \cdot 5$	$\frac{141}{5 \cdot 37} = 26 \cdot 3$	34·
Carbonic acid.....	$\frac{100}{4 \cdot 25} = 23 \cdot 5$	$\frac{141}{6 \cdot 57} = 22 \cdot 2$	21·4

The correspondence is evidently more than accidental, and, regard being had to the conditions of the experiments, quite as close as could be expected. We may therefore take these results of Magnus as an experimental proof of the hypothesis that, with equal constants, the ponderable particles of different gases move with velocities inversely proportional to the square root of their specific gravities; they give, however, no clue as to the numbers of atoms or molecules.

Most authors on chemical physics assume that the absolute temperature (measured from −273° C.) is proportional to the *vis viva*, or working force, of the rectilinear motion of the gaseous particles. It may be shown, however, that in every gas there exists, besides the motion producing heat, some other form of energy, of considerably greater amount, which regulates the fusibility, volatility, and other properties of bodies; this the author designates as *chemical motion*. Thus, 2 litres of hydrogen weigh 0·17878 grm. and 1 litre of oxygen 1·43028 grm. The mean specific heat of both gases is 0·2371, water being taken as unity. At 0° C. both gases have a temperature of 273° C., reckoned from the absolute zero. The three litres contain therefore at 0° C. a quantity of heat = 273 × 1·60906 × 0·2371 = 104·13 units of heat. If the three litres of oxy-hydrogen are burnt, they produce 34·462 × 1·60906 ÷ 9 = 6161·2 units of heat. This heat must have been present in the mixture in some form, since motion cannot be produced out of nothing. On examination we find that heat is never evolved without some corresponding alteration in some of the other properties of the substances, such as their volatility, fusibility, &c., &c. In place of the permanent

gases oxy-hydrogen, we have liquid water. Chemical combination is only the condition, not the cause of the evolution of heat. From the 3 litres of oxy-hydrogen, 6057·07 units of heat have been evolved in excess of those contained as such in the gases. Some form of motion, not in itself heat, must, therefore, in the act of combustion and simultaneous alteration in properties, have been changed into heat. The most simple chemical phenomena will remain inexplicable, if we do not recognise the law of the conservation of force, according to which no motion, and consequently no heat can be generated, but can only appear in consequence of a change in some other previously existing motion. It is, therefore, necessary before attempting an explanation of chemical phenomena, to get familiar with the notion that motions of very great magnitude take place in all substances which, though not actually constituting heat, are changed into it during chemical combination, and are evolved as heat.

R. Clausius (*Deut. Chem. Ges. Ber.*, iv, 269) claims priority with respect to the explanation above given by Mohr, of the greater heat-conducting power of specifically lighter gases, in proof of which he refers to his paper on the heat-conducting power of gases, published in 1862 (*Pogg. Ann.*, cxv, 1; also, *Abhandlungen über die Mechanische Wärmetheorié*, Bd. ii, S. 277). A. D.

On the Law of Avogadro.—The relation of this law—viz., that "equal volumes of different gases contain, under like conditions, equal numbers of molecules,"—to the mechanical theory of gases, has lately been the subject of a somewhat protracted discussion, for which it will be sufficient to refer to the original papers. See A. Naumann (*Deut. Chem. Ges. Ber.* ii, 690; iii, 862; iv, 270); J. Thomsen (*ibid.* iii, 828, 949); Lothar-Meyer (*ibid.* iv, 25); F. Mohr (*ibid.* iv, 78); R. A. Mees *ibid.* iv, 198).

On the Law of Dulong and Petit, with reference to Gases. By F. Mohr (*Deut. Chem. Ges. Ber.* iv, 234).

On the Absolute Magnitude of Chemical Motion (Affinity). By F. Mohr (*ibid.* 237).

On the Force exerted by Detonating Gaseous Mixtures. By M. Berthelot.*

The following table embodies the chief results of the author's investigations on the force exerted by explosive gaseous mixtures:—

* Chem. News, xxiii, 181.

Nature of explosive mixture.	Quantity of heat disengaged by 1 kilo. (1).	Volume of 1 kilo. of mixture (2).		Pressure exerted at the moment of combustion at constant bulk (3) in atmospheres.
		Initial.	Final.	
	Heat-units.	cub. met.	cub. met.	
$H_2 + O$	3,280,000	1·86	1·24	20
$CO + O$	1,570,000	0·75	0·50	24½
$CH_4 + 4O$	2,375,000	0·84	0·84	33
$C_2H_4 + 6O$	2,530,000	0·72	0·72	41
$C_2H_2 + 5O$	2,800,000	0·74	0·63	44½
$C_2H_6 + 7O$	2,300,000	0·70	0·78	39
$C_4H_8 + 12O$	2,450,000	0·63	0·72	46
$C_4H_{10}O + 12O$ (Vapour of ether)	2,400,000	0·59	0·75	49
$C_6H_6 + 15O$ (Vapour of benzene)	2,300,000	0·60	0·63	45
$C_2N_2 + 4O$	2,300,000	0·58	0·58	49½

1. This quantity has been calculated according to the heat of combustion, as adopted in the author's memoir in the Annales de Chimie et de Physique, 4th Series, vol. vi.

2. This volume is taken at a pressure of 760 mm., and at 0° C. The water is supposed to be as vapour; the figures, wherever this occurs, apply only to degrees above 100° generally.

3. This pressure is calculated according to the laws of Mariotte and Gay-Lussac. The following values for the specific heat by constant volume have been taken:—

H_2O = 7·2 for 18 grms.
CO_2 = 7·2 for 44 ,,
N_2 = 4·8 for 28 ,,

It will be seen that the maximum effect produced by exploding the mixtures varies only in the ratio of one to two, and is almost the same amount in the case of all the hydrocarbons. This effect, however, is greater than that of any of the solid or liquid explosive bodies with which we are acquainted. Taking the instance of oxygen and hydrogen, the maximum effect is five times that of gunpowder, and two and a half times that of nitroglycerin. If air be substituted for oxygen the maximum effect does not vary, but the pressure is reduced more than one-half, in consequence of the heat consumed in raising the temperature of the nitrogen. This same reason holds good in the case of nitrous oxide.

The pressure exerted by the explosion of gaseous mixtures is much below that of solids and liquids. To make these equal, it would be

necessary to compress the gases to one thousandth of their initial volume. Such a pressure applied with hydrocarbons would liquefy them, and as the oxygen would remain gaseous, the homogeneity of the mixture would be destroyed, thus rendering an instantaneous explosion by a spark impossible. Berthelot has found that when liquefied nitrous oxide is mixed with liquefied hydrocarbons, mixtures are formed which, for explosive force, vie with nitroglycerin, and the mixtures of potassic chlorate with gun-cotton or potassic picrate. He suggests as examples, mixtures of nitrous oxide with olefiant gas, ether, acetylene or cyanogen.

S. W.

On the Conducting Power of various Metallic Sulphides and Oxides for Electricity as compared with that of Acids and Saline Solutions. By WILLIAM SKEY.*

THE author of this paper points out that great discrepancies exist between his observations and the statements made in works on Electricity. He finds concentrated nitric acid to be the best non-metallic liquid conductor. The following metallic bodies are better conductors than nitric acid:—Mispickel, galena, cuprous sulphide, copper pyrites, ferrous sulphide, tin pyrites, nickel pyrites, bismuth sulphide, magnetic iron ore, graphic tellurium, manganese dioxide, iron pyrites, zinc oxide, &c. Titanic iron and boulangerite were found to be feeble conductors. The following are non-conductors or comparative non-conductors:—Molybdenum sulphide, zinc blende (cryst.), stibnite (cryst.), cinnabar (compact red variety cryst.), orpiment, bouranite (cryst.), manganese blende (not cryst.), proustite, pyrargite, silver-glance, horn silver, ferrous carbonate (black variety, cryst.), calamine, chrome-ore (cryst.), tungstate of iron (cryst.), specular iron ore (cryst.), rutile, bramite, tin ore (cryst.), leverite (cryst.), oxides of copper (cuprous and cupric, cryst.), iserine, copper oxychloride, &c. Mercuric sulphide, whether precipitated and dried, or sublimed, as long as it retains its dark colour, is a good conductor.

S. W.

On the Sensitiveness of the Haloïd Salts of Silver to Light, and the connection of Chemical and Optical Light absorptions. By C. SCHULTZ-SELLACK.†

BY experimenting on the optical absorption of light by means of layers of fused silver chloride, iodide, and bromide, and on the chemical absorption of light by the same substances, Schultz-Sellack has found

* Chem. News, xxiii, 181.

† Deut. Chem. Ges. Ber., iv, 210.

that they accurately agree. It was proved by Draper that all the rays of light which act on a substance chemically, became absorbed.

Schultz-Sellack now finds that "all colours which are optically absorbed to any extent, by a thickness of several millimetres of the silver haloïd salts, bring about chemical decomposition; the absorption of light by these bodies is always connected with chemical action."

It is well known that collodion containing mixed silver bromide and iodide is much more sensitive to light than collodion containing single salts; the parallel is the case with the fused salts, silver iodide is a bright yellow, the bromide a somewhat darker yellow, whilst a mixture of the two when fused possesses an orange-yellow colour. The same is the case when mixtures of bromide and iodide and of iodide and chloride of silver are precipitated; they possess a much higher colour than their separate constituents.

It has been shown that the heat-rays of the spectrum are not absorbed to any extent by haloïd silver salts; it may be then said, that the haloïd silver salts are chemically changed by all rays, which they absorb in perceptible quantity.

A. P.

On the Action of Light on Red Prussiate of Potash. By Dr. H. Vogel.*

It is well known that solutions of red prussiate readily suffer decomposition, yellow prussiate and a blue precipitate being formed. The presence of organic matter facilitates this decomposition considerably. Light seems, however, to be the chief cause. A solution of 1 part freshly prepared ferricyanide of potassium in 10 parts of water, when exposed to diffused daylight, becomes darker in colour in the course of a few hours, while, when it is exposed to direct sunlight, the production of ferrocyanide may be demonstrated by means of ferric chloride, even after the lapse of only thirty seconds. Yellow light is without action on the solution, and no alteration was observed to take place in the solid salt. The action may be made use of for the production of photographic pictures, but this, owing to the unstable character of cyanogen-compounds, is not likely to be of any practical importance at present. Manufacturers may, however, find it advantageous to evaporate and crystallise solutions of red prussiate in the dark, or by lamp light, and chemists should keep their test solution of ferricyanide in bottles of yellow glass.

A. D.

* Deut. Chem. Ges. Ber., iv, 90—94.

On the Action of Light on Mixtures of Alkaline Dichromates and Gelatin. (Abstract of a Communication of Mr. SWAN to the London Photographic Society.)*

MR. SWAN'S conclusions are, that the gelatin film impregnated with potassic dichromate, which is used in "carbon printing" and photolithography, becomes more or less insoluble in those parts which are acted on by light, owing to the reduction of some of the chromic acid to chromic oxide, which then combines and forms an insoluble compound with the gelatin, and not, as is generally supposed, to the oxidation of the gelatin. He finds, in effect, that a solution of a salt corresponding to chromic oxide, produces a leathery precipitate in solutions of gelatin, and that this precipitate is insoluble in both hot and cold water. Mr. Swan further points out that the reduction of the chromic acid may, and to some extent does, generally take place, even in the dark, during the process of drying, and to a greater extent the higher the temperature, but that the difficulty so introduced in practice may be got over by strewing the floor of the drying room with chloride of lime.

C. H. G.

Inorganic Chemistry.

Lecture Experiments. By A. W. HOFMANN.†

Eudiometer with Movable Spark-wires.—The apparatus was suggested by previous experiments on the decomposition of phosphoretted hydrogen. The difficulties to be overcome were the formation of a platinum phosphide when platinum spark-wires were employed, and the difficulties attendant on the construction and cleaning of an eudiometer with fixed carbon points. These difficulties were avoided in the present apparatus by joining two short pieces of glass tube to the eudiometer at right angles, and opposite to each other; on to these tubes are cemented two steel caps; through the latter pass two screws fitting air-tight, the ends of which, passing into the eudiometer, carry stout platinum wires, to which the charcoal points can be attached (the original paper is illustrated by a wood-cut of the apparatus). Sundry precautions, which can more readily be understood by reference to the wood-cut, are required in using the apparatus.

Doubling of the Volume of Carbonic Acid during its Conversion into Carbonic Oxide by the taking-up of Carbon.—This transformation, though so well known, has not hitherto been easily demonstrated. When gas-carbon points are used on the apparatus above described, the decompo-

* Dingl. Polyt. J., cxlv, 130.

† Deut. Chem. Ges. Ber., iv, 243–246.

sition is extremely slow, but by the use of points composed of a mixture of wood-charcoal and sugar-charcoal, a good and rapid result may be obtained. The points are prepared by dipping the platinum wires into a stiff paste of syrup and wood-charcoal; and the wires, to which small portions of charcoal adhere, are now ignited and cooled by plunging under mercury. 20 c.c. of carbonic acid may thus be converted into carbonic oxide in from five to six minutes, and if a more perfect mixture is obtained by alternately increasing and decreasing the volume of the gas by varying the pressure, the time may be even shortened. It is to be noted that new charcoal points are required for each experiment, and that they must be almost in contact.

The experiment is particularly instructive if we start with oxygen instead of carbonic acid. In this case the passage of a single spark ignites the carbon, which then burns until all the oxygen is converted into carbonic acid, and it is demonstrated that the volume of carbonic acid is the same as that of the oxygen from which it is obtained. On now transmitting the stream of sparks the carbonic acid is converted into carbonic oxide, as in the previous experiment.

To reduce the heat generated by the combustion of the carbon in oxygen, it is desirable to increase the volume of the latter by reducing the pressure.

The great success of this experiment for the production of carbonic oxide from carbonic acid, by means of the induction spark between carbon points, suggested a similar experiment for the production of the monosulphide of carbon from the bisulphide of carbon. No such result was obtained, the volume of the bisulphide vapour not undergoing the slightest increase.

E. T. C.

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*Preparation of pure Phosphoretted Hydrogen.**—The ordinary method of obtaining phosphoretted hydrogen gives a mixture of that gas with hydrogen, the amount of the former varying from 15 to 35 per cent. If, instead of using aqueous potash and phosphorus, alcoholic potash is used, better results are obtained; the gas is not spontaneously inflammable, but it is still far from pure. Calcium phosphide on treatment with water gives off a much purer gas, containing only about 13 per cent. of hydrogen; and when hydrochloric acid is substituted for the water, the evolved gas contains about 7 per cent. of hydrogen. The phosphoretted hydrogen obtained from crystallised phosphorous acid contains about 6 per cent. of hydrogen. A perfectly pure gas can, however, be obtained from the action of water, or, better, of potassium hydrate, on the iodide of phosphonium, which can be made with great ease by the pro-

* Deut. Chem. Ges. Ber., iv, 200.

cess described by Baeyer.* The most convenient method of evolving this gas, is to place the iodide of phosphonium in pieces about the size of peas in a flask provided with a delivery-tube, and with a bulb-tube with stopcock passing through the cork in the usual manner. The bulb is filled with potash-solution of about the strength used in combustions, and when the gas is required a few drops are allowed to enter the tube. In this way the evolution can be stopped instantly. The gas thus obtained is perfectly pure, if collected when free from air; it is entirely absorbed by a solution of chloride of lime; it is not spontaneously inflammable, although, on account of its purity, it is more easily ignited than the impure gas containing hydrogen, which has been deprived of its spontaneous inflammability. If it is brought in contact with a drop of fuming nitric acid, it takes fire, as it also does in contact with chlorine or bromine water; by passing the gas through nitric acid which contains a trace of nitrous acid, it becomes spontaneously inflammable. 7·3 grms. of phosphonium iodide will yield about 1 litre of gas.

Decomposition of Phosphoretted Hydrogen by Electric Sparks.—Phosphoretted hydrogen splits up into its components by a series of electric sparks almost as easily as ammonia does. Its decomposition can be shown with almost theoretical accuracy with the gas prepared from iodide of phosphonium. It is most conveniently performed in the eudiometer described formerly;† the only objection to this is that the separated phosphorus combines with the white hot platinum points to a fusible compound, which, by increasing the space between the wires, will sometimes stop the discharge. A U-shaped tube was therefore made, the spark wires of which carried carbon points; by this all difficulty was avoided. 20 c.c. of phosphoretted hydrogen were taken, and after the sparks had passed for 5—6 minutes, 30 c.c. of hydrogen remained, the phosphorus as a brown powder being deposited on the sides of the tube.

A. P.

On the Peroxides Prepared by Electrolysis. By W. Wernicke.‡

The current employed by the author was produced by two cells of Daniell's battery, the positive electrode being a plate of platinum, and the negative consisting of two sheets of platinum, placed one on each side of the positive electrode.

Lead. An alkaline solution of lead and sodium tartrate gave a brilliant, bluish-black deposit of $PbO_2.H_2O$, sp. gr. 6·267. A solution of 1 p. lead nitrate in 8 p. water gave, by 36 hours' treatment, anhydrous PbO_2, sp. gr. 9·045. By treatment for a shorter time, or by

* Ann. Ch. Pharm., clv, 269.

† Deut. Chem. Ges. Ber., ii, 250.

‡ Zeitschr. f. Chem. [2], vii, 85, from Pogg. Ann., cxli, 109.

using more dilute solutions, products are obtained, containing variable quantities of water. It appears that the acid set free at the positive electrode abstracts water from the peroxide, for anhydrous lead peroxide placed in connection with the positive electrode in water containing a little soda, passed into $PbO_2.H_2O$. The quantity of oxygen in the oxide varies inversely as the strength of the current, for by using six elements of Bunsen's battery, pure hydrated lead oxide was formed.

Manganese. The preparation of manganese peroxide requires a weaker current. The acetate and nitrate gave $MnO_2.H_2O$, sp. gr. 2·564.

Bismuth. Two elements of Daniell's battery gave, with a solution of basic bismuth nitrate in sodium tartrate, a black deposit of $BiO_2.H_2O$, sp. gr. 5·571.

Cobalt. An aqueous solution of cream of tartar and hydrated cobalt oxide with a little soda, gave $Co_2O_3.2H_2O$, sp. gr. 2·483.

Nickel. A solution of nickel analogous to that last mentioned, gave $Ni_2O_3.2H_2O$, sp. gr. 2·744.

F. H. H.

Remarks on Ballo's supposed Hydrate of Carbon Bisulphide. By v. Wartha.*

Wartha meets Ballo's criticism (p. 196) by a reference to his (Wartha's) original paper, where the preparation of solid bisulphide in quantity is described by processes which would prevent admixture of frozen atmospheric water with the solid bisulphide.

In return, he considers the experiments which Ballo made in the hope of obtaining solid bisulphide, to be valueless. For instance, by directing a current of air on bisulphide of carbon covered with a layer of absolute alcohol, Ballo observed a lowering of temperature to $-11·5°$, but obtained no solid bisulphide. According to Wartha, this body melts at $-12°$ to $-13°$.

W. H. D.

On the Sulphazotised Acids. By A. Claus.†

Claus has experimented upon a class of acids in which the nitrogen appears to be only partially combined directly with oxygen. They are produced by the action of sulphurous acid on alkaline nitrites. The following five compounds have been accurately experimented upon:—

Potassium Disulphohydrazate, $NOH.2(SO_3K)$, $+ 2H_2O$, forms hard, transparent, colourless prisms, frequently a quarter of an inch long, moderately soluble in warm, almost insoluble in cold water. On heating

* Deut. Chem. Ges. Ber., iv, 180 and 221.

† Deut. Chem. Ges. Ber., iv. 186—190.

with alkalies, only one-third of the nitrogen is obtained as ammonia, thus:—

$$3K_2NHS_2O_7 + 3K_2O = 6K_2SO_4 + NH_3 + N_2.$$

Potassium Sulphohydroxylamate, $NOH_2.SO_3K$, is produced by spontaneous decomposition of the crystallised disulphohydrazate, or by boiling its aqueous solution, or by the action of acids:—

$$NOH.2SO_3K + H_2O = SO_4HK + NOH_2.SO_3K.$$

Hydrogen sulphohydroxylamate, separated from the corresponding barium salt by the action of dilute sulphuric acid, is distinguished from all the other sulphazotised acids, by its stability in presence of free acids. On the other hand, it is decomposed by boiling with excess of potash, all the sulphur being separated as sulphuric acid.

Potassium Sulphazotinate, $NH.NO_2K.4(SO_3K). = K_5N_2HS_4O_{14}$, crystallises in colourless, transparent, rhombic tables. They contain no water of crystallisation, and can be heated to 120° without decomposition. It is soluble in water, with a strong alkaline reaction. Concentrated acids evolve nitric oxide from this salt, from which also only one-third of the nitrogen is obtained as ammonia by distillation with soda-lime. By treating the solution of potassium sulphazotinate with oxidizing agents, as lead dioxide or silver oxide, at 40°—50°, it is coloured intensely blue, and the potassium salt of a new sulphazo-acid is formed, namely:—

Potassic Sulphoxyazotinate, $N_2O_2.4(SO_3K) = K_4N_2S_4O_{14}$. The salt crystallises in intensely yellow needles. The solution is very easily decomposed, losing its colour at the same time. The crystals also decompose, frequently without any assignable reason, and evolve gas, which is partly nitric oxide. On heating them with soda-lime, ammonia is evolved, although from the equation:—

$$K_4N_2S_4O_{14} + 4KHO = 4K_2SO_4 + 2H_2O + N_2$$

there should not be any. The ammonia must be evolved from the next described salt, which is formed by the decomposition of this body.

Potassium Trisulphoxyazate, $NO.3(SO_3K) + H_2O = K_3NS_3O_{10} + H_2O$. This body crystallises in regular rhombic tables, which are colourless and brilliant. It is much more stable than the last body, and can be crystallised from boiling water. On heating with potash, one-third of its nitrogen is evolved as ammonia.

The details of the preparations of these salts are given in the Ann. Ch. Pharm. for April and May, 1871. The sulphoxyazo-compounds are not formed directly by the action of sulphurous anhydride on potassium nitrite with certainty, but a whole series of other salts are formed, which are very unstable.

The action of sulphurous anhydride on potassium nitrite is a simple process of reduction of the nitrous acid, and before the reduction goes so far as ammonia, more or less of the reduced product combines with the group SO_3K produced by oxidation. For the conception of these sulphazo-compounds, the assumption of the pentad nature of nitrogen appears to be absolutely necessary. When sulphurous anhydride is added to potassium nitrite in alkaline solution, it is possible that the two bodies might combine to form SO_2NO_2K, and on a fresh quantity of sulphurous anhydride being added, might again combine to form other more complicated bodies. A. P.

On Ammonium and the Dissolution of Metals without Chemical Action. By Charles A. Seely.*

That ammonium-amalgam is no amalgam at all, but a metallic froth of which the liquid part is mercury, and the gaseous part a mixture of hydrogen and ammonia, is shown by the following facts:—

1st. In the formation of ammonium amalgam the mercury is increased in bulk tenfold or more, while in weight it is increased only one or two thousandths.

2nd. Ammonium-amalgam has less of the mirror surface than mercury; it approaches in appearance to matt silver.

3rd. Ammonium-amalgam is readily compressible; when confined in a fire syringe it steadily contracts on forcing down the piston till the original bulk of the mercury is almost reached, and on relieving the pressure the original volume and appearance are resumed. This forms an effective lecture-room experiment.

The author repeated Weyl's experiments and found that "Weyl has had only an imperfect apprehension of the fundamental facts," (Weyl supposed that he had actually isolated ammonium),† and found that "the key to the whole subject is the fact that liquid anhydrous ammonia is a solvent, without definite chemical action, of the alkali metals." "I mean that these metals dissolve in the ammonia as salt dissolves in water—the solid disappears in the liquid, and on evaporating the liquid the solid reappears in its original form and character. There is no definite atomic action in any such cases, the components of the solution are not changed in their chemical relations to other substances."

An iron retort, filled with anhydrous chloride of calcium, saturated with ammonia at 0° C., had a stout glass tube connected with its turned-down neck by means of a screw coupling. This glass tube served to contain the metal or other substance to be acted on by the ammonia. When sodium is subjected to the condensing ammonia it

* Chem. News, 1871, 169, from Journal of Franklin Institute.

† Pogg. Ann., cxxi, 697.

becomes dark, increases in bulk, becomes pasty, and finally forms a homogeneous mobile liquid, of a lively blue colour, both by reflected and transmitted light. On reversing the process by cooling the ammonia generator, the ammonia gradually evaporates out of the liquid, and the changes observed during the condensation reappear in the reverse order, till at last the sodium is restored to its original bright metallic state. If the evaporation be conducted slowly the metal is left in crystals.

Potassium and lithium behave like sodium. The blue solution of sodium acts as a very powerful reducing agent on metallic salts, and the author anticipates that it will prove of great value for preparing the rare metals. C. H. G.

On the Formation of Rock Salt. By Fr. Mohr.*

During the summer of 1868, an observation was accidentally made which showed the secret of the formation of rock salt. A tall vessel, containing solution of sodium chloride, after standing undisturbed for some months, was found to have some perfectly transparent cubes attached to the bottom. This showed at once that the crystallisation should commence from the bottom, instead of from the top of the liquid, as is generally the case with solutions of sodium chloride. When water has been standing over sodium chloride for some time, it is said to be saturated; but in the case described, a greater concentration must have taken place for the crystals to form at the bottom of the liquid. The conclusion was therefore drawn, that a solution of sodium chloride in contact with such a substance as glass, is able to retain dissolved a larger quantity of salt than when solid sodium chloride is present. An experiment was performed which proved this. A perfectly saturated solution of sodium chloride was weighed, and allowed to evaporate spontaneously; and as soon as traces of crystals showed themselves it was again weighed; 180 grms. of solution lost thus ·282 grm. water, which quantity can dissolve ·102 grm. of sodium chloride. This is the quantity which the solution in contact with glass can retain dissolved above that when in contact with sodium chloride. Crystals formed at the bottom will reduce the surrounding solution to its normal state; it then becomes lighter, and its place is taken by the denser solution from above, and by the diffusion of the liquid the crystals will gradually grow as perfect cubes, and beautifully transparent. The evaporation must be exceedingly slow, or the supersaturation of the liquid at the surface will take place more rapidly than it can diffuse to the bottom, and small crystals will form on the surface of the cubes. On the 31st August, 1868, a cube of rock salt, which weighed 1·120 grm., was placed in a sodic chloride solution; on October 7th it

* N. Repert. Pharm., xx, 146.

weighed 1·492 grm., and was perfectly regular and transparent; on the 7th of January of the next year the crystal weighed 8·9 grms., and was still a cube, but not quite so regular as at first, for the increase had gone on too quickly. The theory of rock-salt formation depends on the fact, that a solution of sodium chloride becomes supersaturated when not in presence of the solid itself.

This kind of phenomenon is not rare; for instance, very dilute solutions of sulphuric acid and barium chloride do not at first precipitate; but when once the precipitation has begun, it increases rapidly on shaking the solution. Another instance is in the formation of magnesio-ammonic phosphate, which can be obtained in crystals several millimetres broad, thus showing the solubility of the salt when there is none of the solid present. A. P.

On the Formation of Transparent Cubes of Sodium Chloride.
By L. A. Buchner.*

Whilst Mohr has experimented on the formation of cubes of sodium chloride in solutions of the pure salt, Buchner has investigated its crystallisation from mixtures of salts. He agrees completely with Mohr as to the conditions for obtaining transparent salt cubes, and also finds that the presence of certain hygroscopic bodies, rather increases than diminishes the tendency to form perfect crystals. An experiment described serves to show this. Solutions of ferric chloride and sodium chloride were mixed and concentrated; on cooling, some of the sodium chloride crystallised out; the thick mother-liquors were separated and placed in a dish covered with paper. After standing a few weeks, some perfectly regular, transparent, and colourless cubes were found at the bottom. In this case the concentrated solution of ferric chloride cannot evaporate, but, as is well known, it absorbs moisture from the air. Buchner thinks that this tendency of the ferric chloride causes a supersaturation in the lower layers of the solution, as regards the sodium chloride, and thus crystallisation begins from the bottom. Magnesium chloride has also the same action. By the very gradual evaporation of a solution which contained several salts as well as a precipitate of Prussian blue, small, perfectly regular, and colourless cubes of potassium chloride were obtained. The gradual evaporation of a solution containing cupric chloride and ammonium chloride has also yielded small crystals of ammonium chloride, which were not only transparent, but perfectly colourless. The conditions of crystals of formation of the potassium and ammonium chloride seem to be the same as in the case of sodium chloride. In these experiments the extremely sharp separation of salts by crystallisation has been most clearly shown.

A. P.

* N. Repert. Pharm., xx, 151.

On the Behaviour of certain Lithium Minerals before the Spectroscope, and on the occurrence of Thallium in Sphalerite from Geroldseck (Breisgau). By v. KOBELL.*

THE author finds that some minerals containing lithium, although producing an intense coloration of the blow-pipe flame, give no corresponding indication with his spectroscope unless ignited, powdered and treated with hydrochloric acid, whilst others, although colouring the flame but slightly, develope the lithium lines before his spectroscope without such preliminary treatment.

Cookeite from Hebron, lithionite from Rozena, Chursdorf, Elba, Ural, Paris and Utön, belong to the latter class, whilst asbolane from Saalfeld, psilomelane from Schneeberg, Sayn and Siegen, lithionite from Zinnwald and Altenberg, amblygonite from Hebron, although colouring the blow-pipe flame more or less deeply, give no lines with the author's spectroscope, unless treated in the manner before mentioned. All lithium minerals, however, if powdered and treated successively with ammonium fluoride, sulphuric and hydrochloric acids give lines before the author's spectroscope.

The difference in the behaviour of these minerals is not owing to differences in the quantity of lithium, fluorine or water, and varies with the spectroscope employed.

Sphalerite from Schemnitz, Lauterberg (Harz), Freiberg, Raibel (Carinthia), Obernhof (Nassau), Vordernberg (Tyrol), Rauschenberg (Bavaria), New Bethlehem (Pennsylvania), did not give the slightest indication of the presence of thallium, but the dense variety (Schaalenblende) from Geroldseck (Breisgau), gave a distinct reaction, and a similar specimen from Herbesthal (Westphalia), a weaker indication of this metal. The examination was made by heating the finely powdered mineral on platinum foil before the spectroscope.

F. H. H.

On the Amount of Copper in Iron. By C. RUMP.†

FROM the researches which Rump has made he believes that the purest iron of commerce is not perfectly free from traces of copper; in one case the quantity amounted to 0·1 in 100 grms., in many others only traces of copper can be found. If iron containing copper is dissolved rapidly in hydrochloric acid, a part of the copper will also be dissolved, and can be precipitated of a brown-red colour by sulphuretted hydrogen. If the precipitate is black, it shows that the iron probably contained lead. In one sample of iron used in pharmacy, no

* Journ. pr. Chem. [2], iii, 176.

† Arch. Pharm. [2], cxlv, 231.

trace of copper was found, but in some "iron powder" examined, there were more than traces of copper, as well as lead, found in it.

A. P.

On the Decomposition of Silver Iodide. By A. VOGEL.*

ON boiling silver iodide with potassium hydrate, its yellow colour changes into a grey; no decomposition, however, takes place, for no potassic iodide is found in solution. The change seems, therefore, to be a molecular rather than a chemical one. Silver iodide is, indeed, rather difficult to decompose, for on melting with potassium hydrate, only a very incomplete decomposition takes place; the same is the case with its reduction by means of zinc and hydrochloric acid; complete decomposition of all the silver iodide frequently does not take place, but it remains with the metallic silver. The affinity of iodine for silver seems therefore stronger than that of chlorine; when dry silver chloride is rubbed with iodine, and, after standing some time, the excess of iodine is removed by washing with alcohol, silver iodide is partially formed, for the salt remaining is not wholly soluble in ammonia. When silver iodide is fused, slight decomposition takes place, a small quantity of iodine being liberated; on stronger heating with a blowpipe, its smell is quite perceptible. It can also be sublimed. This is best performed by mixing the silver iodide with finely powdered quartz sand, and heating the mixture strongly. The change of colour which silver iodide undergoes when heated can be shown as a lecture experiment, by saturating strong filter-paper with silver solution, and then with solution of potassium iodide; on carefully heating the bright yellow paper over a lamp, it changes to a dark orange-yellow; when cooled by blowing on it, or by contact with the finger, it recovers its original colour. The experiment is also conveniently performed by making a thin plate of a mixture of plaster of Paris and silver iodide; on heating, the usual change of colour takes place.

A. P.

On some new Sulpho-salts. By R. SCHNEIDER.†

Sodium Sulphopalladate and Palladium Disulphide.—By fusing together one part of yellow ammonium-palladium chloride (or half a part of palladium monosulphide) with twelve parts of dry sodium carbonate and twelve parts of sulphur, and keeping the mixture fused for ten minutes, over a blowpipe lamp, a reddish brown homogeneous mass is obtained, which dissolves in water to a clear deep brown solution, leaving a small light grey metallic looking residue,

* N. Repert. Pharm. xx, 129.

† J. pr. Chem. [2], iii, 103—120, from Pogg. Ann., cxli, 519.

consisting of fine needles. On adding hydrochloric acid to slight acid reaction, the solution deposits a light chocolate-brown precipitate, containing much sulphur, but chiefly palladium disulphide, and forming sulpho-salts (sulphopalladates) analogous to the platinum and iridium sulphides. Sulphopalladates may in fact be obtained under favourable conditions in the solid form—some even in the crystalline state—by fusing together one part of yellow ammonium-palladium chloride (or half a part of palladium monosulphide) with only six parts of dry sodium carbonate and six parts of sulphur. A mass is left which on cooling shows a net-work of brown needles, soluble in water, and cannot therefore be obtained readily in the pure state; they are, however, insoluble in absolute alcohol, and by lixiviating the coarsely powdered mass with alcohol, the sodium polysulphide is dissolved out, but not the sodium sulphate, which is invariably found to a considerable extent in the fused mass, and is but slowly washed out by weak alcohol, as it is impossible to prevent the partial oxidation of the moist palladium compound, indicated by the appearance of a little palladium hyposulphite in the alcoholic washings.

The analysis of this compound led to the formula $Na_2S.PdS_2$, which the author confirmed by decomposing the sodium sulphopalladate by means of silver nitrate, in a manner similar to that which had been successfully followed in the determination of disodium sulphoplatinate, according to the reaction:—

$$Na_2S.PdS_2 + 2AgNO_3 = 2NaNO_3 + Ag_2S.PdS_2.$$

The precipitate agreed with the formula of silver sulphopalladate $Ag_2S.PdS_2$, and as the silver had evidently replaced the sodium in the sulpho-salt, the composition of the latter must be expressed by the formula $Na_2S.PdS_2$, or $Pd^{iv}\left\{\begin{matrix} S'' \\ (NaS)_2 \end{matrix}\right.$, or $S{=}Pd\left\langle\begin{matrix} SNa \\ SNa \end{matrix}\right.$, in which the metal palladium evidently acts as a tetrad element.

The new sulpho-salt appears to form thin, somewhat flattened, brown or reddish lead-grey needles, having a feeble metallic lustre; when seen in thin layers under the microscope, they appear transparent with a reddish brown tint, and when pressed with a glass rod, show a yellowish brown streak. They are somewhat difficultly soluble in water, forming a deep reddish brown solution, but perfectly insoluble in alcohol. The aqueous solution becomes rapidly oxidized when exposed to the air, with partial separation of palladium sulphide.

The light chocolate-brown precipitate already referred to, obtained by saturating the aqueous solution of the fused mass with hydrochloric acid, consists of a mixture of palladium disulphide and sulphur, which may be freed, though with difficulty, from the last traces of sulphur by extraction with carbon disulphide. The palladium disulphide can,

however, be prepared in the pure state by fusing the monosulphide with three parts of sodium carbonate and three parts of sulphur, pulverising, and exhausting the mass thoroughly with alcohol, and decomposing the residue with dilute hydrochloric acid. Sulphuretted hydrogen is evolved, and a bulky spongy precipitate is left which when washed and dried, has the composition of palladium disulphide, PdS_2. It constitutes a stable, dark blackish-brown, rather dense crystalline powder which, under the microscope, still shows distinctly the needle form of the sulphopalladate crystals from which it had been extracted. When gently heated in an atmosphere of carbonic anhydride it yields a sublimate of sulphur and palladium monosulphide; the latter, when the heat is increased, is converted into the more stable palladium subsulphide, which melts, but does not lose its sulphur completely, when heated even very strongly over the blowpipe flame.

Boiling nitric acid attacks palladium disulphide, but the action appears to be confined to the partial oxidation of the sulphur only, since the solution acquires merely a light yellow tint. Aqua regia dissolves it rapidly and completely without separation of sulphur.

Potassium Sulphopalladate and Palladium Subsulphide.—The anticipation that the potassium compound corresponding to the sodium sulphopalladate would be formed on fusing together ammonium palladium chloride with potassium carbonate and sulphur was not realised: for the sulpho-salt, so obtained, is quite insoluble in water, and the mass appears to contain potassium sulphide and palladium disulphide, together with palladium subsulphide, Pd_2S, as an essential constituent.

Two parts of ammonium-palladium chloride (or one part of palladium sulphide) when fused for ten minutes over a blowpipe lamp with 12 parts of pure potassium carbonate and 12 parts of sulphur, yielded a mass which dissolved for the most part, when treated with water, to an intensely brown liquid,* and left numerous very thin six-sided minute plates of vivid metallic lustre and brilliant violet blue colour.

The upper, and frequently also the lower layer of the fused mass usually holds embedded somewhat larger plates of distinct crystalline structure. On washing with water, these crystals are readily obtained perfectly pure. They have, when dry, a steel-blue lustre.

This beautiful compound resembles potassium sulphoplatinate, described by the author on a former occasion, but is of essentially different composition. Its analysis leads to the empirical formula $K_2Pd_3S_4$, and judging from the crystalline appearance, the author thinks

* From this liquid, which contained, besides some considerable quantities of potassium sulphopalladate, a large excess of potassium polysulphide, hydrochloric acid precipitates palladium sulphide, which may be employed for fresh fusions.

that, as there can be little doubt that the compound contained palladium disulphide, besides potassium sulphide, the rational formula should be written $K_2S.Pd_2S\}PdS_2$, which would render probable the existence of palladium subsulphide, corresponding to the suboxide, discovered by Kane. This was, moreover, shown by the fact that the subsulphide can be readily obtained in the pure state under conditions which render it probable that it plays an essential part in the formation of the blue sulpho-salt in question: for palladium disulphide can be exposed to the high temperature at which the fusion has to be effected, only in the form of an alkaline sulphopalladate, whereas when heated by itself with equal intensity, it loses sulphur and is converted into palladium subsulphide. Taking the formula $K_2S.Pd_2S\}PdS_2$ to be the correct expression for the blue sulpho-salt, it may be assumed that by reducing the amount of potassium sulphide in the fused mass, the quantity of palladium disulphide would be diminished, and that of the subsulphide correspondingly increased; and that under certain conditions it would be possible to obtain almost the whole of the palladium in the fused mass as subsulphide. This was effected by fusing together for 15—20 minutes, at a bright red heat, over the blowpipe lamp, an intimate mixture of one part of ammonium-palladium chloride (or $\frac{1}{2}$ part of palladium monosulphide) with six parts of potassium carbonate,* six parts of sulphur, and three parts of sal-ammoniac. The latter forms with the potassium carbonate, potassium chloride, and thereby diminishes the amount of potassium sulphide in the fused mass. The latter is at the same time rendered less fluid, whereby the volatilisation of the excess of sulphur and the conversion of the palladium disulphide into subsulphide is considerably facilitated.

The cold mass yields, on treatment with water, a light yellow solution, which contains no potassium sulphopalladate. The insoluble portion consists of a greyish brittle regulus, together with a very trifling amount of blue sulphopalladate, which can be separated by levigation. Analysis showed the regulus to be composed of palladium subsulphide, Pd_2S. The author several times obtained hard and brittle reguli of the size of a small pea, which could be readily reduced to an ash-grey powder. They exhibited a metallic greyish-white fracture and a fine crystalline grain. Their specific gravity at 15° C. was 7·303. Palladium subsulphide is not attacked by simple acids; even aqua regia attacks it but slightly. When heated to redness, it melts to brilliant little globules, which lose sulphur very slowly, even when exposed to the heat of a blow-pipe flame. They lose their brittleness in proportion as they yield up their sulphur and can then no longer be reduced to a powder, but retain traces of sulphur even after long-continued ignition. It is therefore impossible to reduce the sulphides of palladium to

* An equal quantity of sodium carbonate may also be substituted.

metallic palladium by mere roasting to ignition. The same has been observed previously by H. Rose.*

Heated in a current of hydrogen, palladium subsulphide is decomposed slowly and with difficulty. The reduction begins only at a red heat, and proceeds so slowly that traces of sulphuretted hydrogen come off after heating even for hours.

After what has been stated regarding the formation and the deportment of palladium subsulphide, it is rendered all but evident that it forms a proximate constituent of the blue sulphopalladate. The author thinks it conceivable, however, that the palladium monosulphide—present from the first in the fusion or formed subsequently thereto—undergoes decomposition at a higher temperature, under the disposing influence of the potassium sulphide, according to the equation, $3PdS = Pd_2S + PdS_2$, and that both the palladium subsulphide and disulphide enter simultaneously into combination with potassium sulphide to form the blue sulpho-salt represented by the formula, $K_2S.Pd_2S\}PdS_2$,

$$\left.\begin{matrix} K_2 \\ \text{or } Pd^{iv} \\ (Pd_2)'' \end{matrix}\right\} S_4, \text{ or } \begin{matrix} K{-}S \\ \\ K{-}S \end{matrix}\!\!>\!Pd\!<\!\begin{matrix} S{-}Pd \\ | \\ S{-}Pd \end{matrix}$$

in which the group Pd_2 acts as a dyad element.

Potassium-palladium sulphopalladate forms hexagonal plates, which, when seen under water, appear brilliant violet-blue, and when dry, steel-blue, and so flimsy, that a breath of air blows them away. They have a bright metallic lustre. When seen under the microscope, in very thin layers, they appear transparent and are of yellowish-brown to dark reddish-brown colour. They are perfectly constant in air and are insoluble in cold as well as in hot water. Heated out of contact with air, they bend and twist and acquire a peculiar whirling motion. When suddenly exposed to a strong heat, they emit sparks and fall into smaller fragments, but undergo no further decomposition, since the sparks are neither accompanied by liberation of free sulphur nor by any evolution of gas. On heating them in a current of hydrogen, the same phenomena are observed at first, and a partial reduction takes place, accompanied by evolution of sulphuretted hydrogen. By raising the temperature ultimately to bright redness, nearly half the sulphur is driven off. The reduction was never accompanied by formation of water. The reduced mass appears, after cooling in a current of hydrogen, as a reddish-brown powder, interspersed with greyish-white dull lustrous spots. It is partially soluble in water free from air, forming a deep brown liquid. The solution has a strong alkaline reaction and a marked hepatic odour, and contains nearly the whole of the potassium and about $\frac{1}{5}$th of the palladium present in the

* Traité de Chimie Analytique, ii, 317.

compound. It readily deposits palladium disulphide on addition of hydrochloric acid.

The portion insoluble in water forms a dense greyish-black powder, consisting principally of metallic palladium, usually mixed with a little palladium sulphide in the form of a loose black powder—probably in consequence of the aqueous solution of the alkaline sulphopalladate having undergone a partial decomposition by exposure to air before and during filtration.

The author expresses these changes by the equation—

$$2(K_2S.Pd_2S\}PdS_2) + 8H = 4H_2S + 2K_2S.\ PdS_2 + 5Pd,$$

which, however, is not borne out very closely by experimental numbers.* The aqueous extract of the reduced mass contained four atoms of potassium to one atom of palladium, corresponding to the above atomic proportions.

It would appear that a portion of the palladium disulphide of the original compound, existing as basic potassium sulphopalladate, $2K_2S.PdS_2$, resists the reducing action of the hydrogen, like the sodium sulphantimoniate, which resists strong ignition in a current of hydrogen, whilst antimonic sulphide is readily reduced.

Heated with moderately concentrated hydrochloric acid, potassium-palladium sulphopalladate speedily loses its blue colour and assumes a dark steel-grey tint, gradually giving up the whole of the potassium to the acid. It is remarkable that none or mere traces only of sulphuretted hydrogen or hydrogen are given off, even on heating. The hydrochloric acid extract contains only potassium chloride and is free from palladium. The author proposes to investigate this interesting reaction further.

The compounds above described are the first examples of sulpho-salts of palladium, and as such are of some interest, as their study has led to the isolation and more accurate knowledge of two hitherto unknown sulphides of palladium—the subsulphide and the palladium disulphide.

Palladium is usually regarded as a positive metal, mainly on account of the insolubility of palladium sulphide in ammonium sulphide. The fact of its forming true sulpho-salts is little favourable to this view; it proves on the contrary, that, like platinum, this metal possesses a more negative character.

C. Clauss, whose investigations of the platinum metals are so well known, places palladium in his classification at the negative end of the collateral series, where it is united with the corresponding member in

* This discrepancy he ascribes to the action of the potassium sulphide upon the glass. He explains the reduction of the corresponding potassium-platinum sulphoplatinate, described by him on a former occasion, in a sense similar to that which he advocates.

the main series,—the metal platinum,—constituting with the latter a pair of elements, which are brought into closer relation to each other by numerous analogies. W. V.

Mineralogical Chemistry.

On some Rocks and other Dredgings from the Gulf Stream. By S. P. Sharples.*

Specimens of rock, ooze, and semi-fossilised bone, obtained by dredging from the bed of the Gulf Stream between Florida and Cuba, were carefully analysed, and the results compared with the analyses of more recent specimens of the same material.

The fossil bone was almost destitute of organic matter, and contained as its principal constituents 62·4 per cent. of calcium phosphate and 26·47 per cent. of calcium carbonate. The analyses of recent bone, also free from organic matter, gave 92·79 per cent. of phosphate and only 7·21 per cent. of carbonate. The fossil bone contained also an appreciable amount of iron.

The analyses of the rock, mud, &c., showed that they were evidently of osseous origin, but more or less contaminated with corals and shells. In these specimens the calcium phosphate had likewise been to a considerable extent replaced by carbonate, while magnesia had taken the place of part of the lime.

	Rock 1.	2.	3.	Ooze.
$CaCO_3$	36·5	47·11	96·96	85·62
$Ca_3P_2O_8$	35·54	13·15	1·20	0·18
$MgCO_3$.....	10·56	12·39	—	4·26

With respect to this replacement of phosphate by carbonate, one or two explanations are offered. Calcium phosphate is soluble to a considerable extent in solutions of organic matter (a fact which the author had confirmed by special experiments), which would account for the removal of part of that salt. Again, during the decomposition of the gelatin of the bone, ammonium carbonate would be formed in considerable quantity, and this latter salt would decompose calcium phosphate more or less completely; we should therefore have ammonium phosphate going into solution, while calcium carbonate would be deposited.

The origin of the iron in these specimens is doubtful, but it is supposed to be derived from ferruginous particles carried down by the great rivers which empty themselves into the Gulf of Mexico.

A few corals were examined and compared with recent corals, mainly with reference to the phosphoric acid they contain. The result was

* Sill. Am. Journ. [3], i, 168.

that while the coral treated in a fresh state gave a strong reaction, the fossil specimens were almost free from phosphoric acid.

J. W.

Winkworthite, a new Mineral from the Gypsum of Hants County, Nova Scotia. By Prof. How.*

Among some reputed specimens of Howlite (silicoborocalcite) from the Winkworth gypsum quarries, the author found two nodules of unfamiliar appearance, which proved to be a mineral containing sulphuric acid, in addition to the ordinary elements of silicoborocalcite.

The first nodule was a colourless, transparent mass, coated with small colourless crystals of considerable lustre. The fracture was nearly flat, and new surfaces were covered with glistening, irregular facets. With the microscope, transparent, oblique-angled plates were observed. The hardness of the interior was about 3, that of the exterior about 2. An analysis of the air-dried mineral gave these results.—Water 18·80; lime 31·66; sulphuric acid 36·10; silicic acid 3·31; boracic acid (by difference) 10·13. These numbers accord closely with the following equivalent ratios:—

$$11CaO,\quad SiO_2,\quad 9SO_3,\quad B_2O_3,\quad 20H_2O.$$

The second nodule had not so crystalline an exterior as the above, but in its general characters closely resembled it. Its hardness was a little above 3. Before the blowpipe it, like the first nodule, coloured the flame green. In an analysis of the air-dried mineral, a little carbonate of lime was found; its amount (4·47 per cent.), calculated from the quantity of carbonic acid, has been deducted from the following results of its examination:—Water 18·00; lime 31·14; sulphuric acid 31·51; silicic acid 4·98; boracic acid (by difference) 14·37. These numbers correspond with the following equivalent ratios:—

$$11CaO,\quad SiO_2,\quad 8SO_3,\quad 4B_2O_3,\quad 20H_2O.$$

The new species is intermediate between selenite and silicoborocalcite, and may originate from the reaction of their elements during or after deposition. The nodular form, characteristic of howlite as distinguished from the crystalline habit of selenite, seems to show that the former was the original deposit, in which case winkworthite would be a product of its alteration by selenite. Nodules of selenite occasionally occur in the gypsum beds at Winkworth, exactly resembling the amorphous kinds of the borates, of which they are probably pseudomorphs. Several specimens of howlite were examined for sulphuric acid; in some cases mere traces were present, both in the hard crystalline and the soft opaque conditions of the mineral; while in other specimens, respectively similar, the quantity was decided and some-

* Phil. Mag., 1871, 270.

times considerable, even after every precaution has been taken to exclude selenite, which is often present in bands traversing the borate.

W. F.

The Melaphyres of the Little Carpathians. By H. Höfer.*

The melaphyre of this district is an eruptive rock of the middle trias period. The author has arranged the results of his investigations of this group under the four following heads: the compact, the crystalline, the porphyritic, and the amygdaloïdal.

The Compact Melaphyre.—This is the predominating variety of this group, and is distinguished by its varied colour, the darker hues, however, prevailing. The typical colour is black, with a dash of violet; red and reddish-brown are rare, and black passing into green is frequent. By weathering, the latter hue changes to a light yellowish-brown, through the oxidation of iron protoxide. The green varieties effervesce more with acid than the black, and this is especially the case with freshly-exposed dark green specimens. The green melaphyre takes a black colour and almost metallic lustre by weathering. By aid of a lens, numerous dark green granules, resembling seladonite, are observed in it. Compact melaphyre melts before the blowpipe to a black and very vesicular slag; has a stony conchoïdal fracture, and a hardness between 6 and 7. Though hand specimens but slightly affect the magnetic needle, this instrument is entirely untrustworthy in the vicinity of the rocks themselves. The specimens examined were: I. Violet-black melaphyre, from the southern end of the Blumenthal, north of Grenitz; spec. grav. 2·852. II. Blackish-grey melaphyre, with a dash of olive-green, resembling basalt, from the bed of the Schwarzen Waag, near Hoskowa; spec. grav. 2·734:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	CO_2.	H_2O.	
I. *a*.†....	52·75	10·80	20·24	3·84	2·36	0·41	1·54	3·62	1·99	3·10	100·65
I. *b*.‡....	55·20	11·30	21·18	4·02	2·47	0·43	1·61	3·79	—	—	100·00
II. *a*.....	50·41	21·40	11·07	4·95	3·31	0·94	2·26	3·91	—	3·33	101·58
II. *b*.....	51·31	21·78	11·26	5·04	3·37	0·96	2·30	3·98	—	—	100·00

The oxygen ratios of silica, sesquioxides, and protoxides are in I*b*: 29·438, 11·629, 3·009; and in II*b*: 27·364, 13·556, and 3·865.

The crystalline melaphyre is in a state of transition from the compact to the porphyritic variety; bright coloured scales separate themselves

* Jahrbuch für Mineralogie, &c., 1871, 113.

† The actual numbers resulting from each analysis are given under *a*.

‡ The percentages, given under *a*, are here raised to 100, after carbonic acid and water have been deducted.

from the uniform mass, and when of some size are recognized as felspar; the conchoïdal fracture is lost, and becomes irregular. If the crystals of felspar increase in size, the rock is then porphyritic, and the three forms of melaphyre are occasionally met with, side by side, *in situ*. The lithological characters of the crystalline are, as regards colour, as varied as those of the compact melaphyres, to each of which, in fact, a congeneric crystalline kind is to be met with.

The specimen examined was from the Ipolticzathal, near Hoskowa. It was green; had a spec. grav. = 2·859, and enclosed very small white brilliant crystals, apparently of felspar, green, often foliated, masses, intimately mixed with the felspar, and occasional black, angular granules. Its composition is—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	
a.	48·69	12·81	10·77	9·43	7·99	0·99	1·66	5·56	3·36	99·26
b.	50·77	13·36	11·23	9·84	8·33	1·03	1·73	3·71	—	100·00

The oxygen ratios of silica, sesquioxides, and protoxides are—27·076, 9·610, and 6·203.

The porphyritic melaphyre.—The dark varieties and those with a violet hue are, with scarcely an exception, the only ones which become entirely porphyritic. This division, therefore, is characterised by a blackish-violet base, enclosing greenish felspar in crystals, on an average 6 lines in length and 1‴ in breadth.

The composition of a specimen of the above kind, found south of Luczivna, at the north foot of the Palkniczaberg, is given below (I), as well as that of the light green felspar (andesin) which it encloses (II), and the dark violet base itself (III).

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	NaO.	H_2O.		Sp. gr.
I *a.* ..	52·46	19·65	10·86	1·92	5·30	0·65	1·57	2·89	4·81	100·11	2·689
I *b.* ..	55·05	20·62	11·40	2·01	5·56	0·68	1·65	3·03	—	100·00	—
II *a*...	53·26	24·28	—	2·96	6·83	0·56	2·47	4·68	3·98	99·02	2·633
II *b*...	56·04	25·55	—	3·12	7·19	0·59	2·59	4·92	—	100·00	—
III *a*..	50·65	16·32	15·03	2·33	4·45	0·63	1·79	3·44	5·14	99·78	2·751
III *b*..	53·52	17·25	15·88	2·46	4·70	0·67	1·89	3·63	—	100·00	—

The oxygen ratios of silica, sesquioxides and protoxides are—I*b*, 29·358, 13·139, and 3·352; II*b*, 29·886, 11·943, and 4·681; and III*b*, 28·542, 12·822, and 3·397.

A further example of this variety, from an entirely isolated out-crop in the Bistrathal, near Bries, enclosed green crystals of felspar, and

round masses, 1½ lines across, of a green, almost compact mineral, which was found to be delessite, and wherein lay small particles of calcite. This rock has a pretty even splintery fracture, and is probably in the first stage of decomposition. Its specific gravity is 2·816, and composition—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	CO_2.	H_2O.	
52·21	12·84	16·35	5·67	3·67	1·13	0·98	1·90	2·01	4·50	101·26
55·10	13·55	17·26	6·00	3·87	1·19	1·03	2·00	—	—	100·00

The oxygen ratios of silica, sesquioxides, and protoxides are—29·385, 11·506, and 3·589.

The amygdaloïdal melaphyre. The numerous varieties of this group agree in having a dark base. In one from the Nischne Chmelenicthal, at Svarin, it was of a dull dirty violet, and enclosed felspar crystals 1½ lines in length, which had lost their distinct cleavage, were without lustre, and effervesced with acid. In some of the more altered crystals small spherules of a dark green mineral are seen; in other instances the entire structure of a crystal has been replaced by this substance. The amygdaloids, then, are clearly due to a metamorphosis of the andesin.

The specific gravity of this altered melaphyre is 2·856, and its composition is given below, under I.

A typical specimen from Schwarzwaag had a dull reddish-brown base, enclosing delessite, amygdaloids of calcite, and here and there small particles of mesitin. The felspar was completely decomposed. Its specific gravity is 2·727, and composition as under (II) :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O	CO_2.	H_2O.	
I *a*. ..	51·80	7·78	20·99	5·34	3·10	0·47	2·25	2·71	1·29	3·77	99·50
I *b*. ..	54·85	8·24	22·23	5·65	3·28	0·50	2·38	2·87	—	—	100·00
II *a*...	42·75	14·04	14·10	2·50	9·10	0·57	2·22	4·29	7·69	3·49	100·75
II *b*...	47·73	15·67	15·74	2·79	10·16	0·64	2·48	4·79	—	—	100·00

The oxygen ratios of silica, sesquioxides, and protoxides are—I*b*, 29·252, 10·514, and 3·523; and, II*b*, 25·454, 12·042, and 5·411.

The minerals met with in the larger cavities of the altered melaphyre of this region are—delessite and green earth, calcite, mesitin, quartz, chalcedony, agate, and jasper, pistacite, heulandite, copper pyrites, and malachite. W. F.

A New Locality for Monazite (Turnerite). By G. VOM RATH.*

IN a cavity of a sanadine bomb from the Lake of Laach, the author observed a crystal of orthite on which lay another crystal, 1 mm. in length, olive green in colour, and with a brilliant lustre; the latter he identified with monazite, a mineral hitherto unknown not only at Laach, but in any volcanic rocks whatever. Vom Rath believes the Laach crystal, which, from its minute size, he was unable to analyse, to be monazite, its immediate association with the orthite rendering it highly probable that it also is a cerium compound. The crystal is tabular, and exhibits the following combinations: . $\infty \breve{P} \infty$. ∞P. $-P\infty$. $P\infty$. $\infty \breve{P} \infty$. $\breve{P}\infty$. P. The goniometric measurements were, $\infty P = 86° 25'$; $\breve{P}\infty : \infty P = 115° 44'$; $\breve{P}\infty : \infty P = 109° 18'$. The directions of cleavage of the Laach crystal also accord with those of monazite. A strong lustre arising from internal fissures is seen along the edges of the positive and negative hemidomes, and indicates a distinct direction of cleavage parallel to the base, which does not form a face of the crystal. There is a second cleavage parallel to the orthopinacoïd. Monazite has hitherto been found either in the old plutonic rocks or in alluvium derived from them; its mode of occurrence in the Lake of Laach therefore is peculiar. It furnishes a second instance where a mineral containing cerium has been found in volcanic masses, and is an instructive example of mineral association, that of orthite with cerium phosphate. The earlier laws, held to be to some degree trustworthy, respecting the geological distribution of minerals lose some of their significance. Oxide of cerium was supposed to be present in the oldest plutonic rocks only, never in the volcanic. Vom Rath, however, has found orthite at Laach and Monte Somma, and monazite in the Laach sanidine. If we include in this category the turnerite from Tavetsch and the Dauphiné, the mineral in question, the cerium lanthanum phosphate, brings into intimate association the three different formations: the crystalline slates, the old plutonic, and the volcanic rocks.

W. F.

Analyses of Nephrite and Saussurite. By L. R. v. FELLENGBERG-RIVIER.†

ONE specimen of nephrite (I) is the hilt of a sword, brought from the East. Its specific gravity is 2·978 and hardness between 6 and 7. Its fracture splintery and colour greenish-white. The second (II) was found at a place of burial in Irkutsk, East Siberia, from 8 to 10 feet

* Jahrbuch für Mineralogie, &c., 1871, 172.

† Jahrbuch für Mineralogie, &c., 1871, 173.

below the surface in sandy soil. Its specific gravity is 3·019 and its colour dark grey in reflected and a bright grass-green in transmitted light, the latter hue being ascribed to chromium oxide.

	SiO_2.	Al_2O_3.	FeO.	MnO.	Cr_2O_3.	CaO.	MgO.	H_2O.	
I.	58·10	4·30	1·89	0·28	—	13·24	24·18	1·20	100·09
II.	57 1	0·96	4·86	0·28	0·33	13·64	22·22	1·60	100·00

These analyses confirm v. Fellengberg's former view that nephrite is to be regarded as a silicate of lime and magnesia, whose components vary within narrow limits, small quantities of the two bases being replaced by vicarious oxides, most of which are coloured. The alumina indicates the presence of a foreign silicate of this base, which may perhaps be detected by microscopic examination.

The wedge of saussurite had the form of a chisel, and was found in a lake-dwelling on the Lake of Bienne, between Gerlafingen and Hageneck. Its fracture is splintery, hardness 6·5, and specific gravity 3·407. It is but slightly translucent, is light sea-green in colour, and is thus composed :—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	Na_2O.	H_2O.	
48·86	29·27	1·67	11·74	5·43	3·58	0·50	= 100·05

With the exception of that occurring *in situ* in Switzerland, and some found in erratic blocks, all the saussurite met with in wrought forms is imported from the East.

W. F.

Gümbelite, a new Mineral. By F. v. Kobell.*

At Nordhalben, near Steben, in Upper Franconia, this mineral forms thin fibrous layers on clay slate, or on the iron pyrites, which occurs in small flattened masses. It is greyish-white, of a soapy to pearly lustre, translucent, soft, and pliant, and feels, when rubbed like fine asbestos. It intumesces before the blowpipe, and the fine fibres fuse into a mass resembling porcelain. It gives off water when heated, and resists the action of acids. Its analysis gave the following numbers :—

SiO_2.	Al_2O_3.	FeO.	MgO.	K_2O.	H_2O.	Undecomposed. substance.	
50·52	31·04	3·00	1·88	3·18	7·00	1·46	= 98·08

W. F.

* Jahrbuch für Mineralogie, &c., 1871, 174.

Lüneburgite. By C. Nöllner.*

Some crystals that separated from the mother-liquor of sea-water, the source of which is not given, were observed to contain not only boracic acid, but phosphoric acid also, like the stassfurtite and lünebergite recently found at Lüneberg. They had the following composition:—

MgO.	P_2O_5.	B_2O_3.	H_2O.	
25·3	29·8	12·7	32·2	= 100·0

It likewise contained about 0·7 per cent. of fluorine. The formula to which the above numbers correspond is—

$$[(2MgO.H_2O)P_2O_5 + MgO.B_2O_3] + 7H_2O.$$

W. F.

Saponite, from Fohnsdorf, in Styria. By K. v. Hauer.†

The brown coal met with at Fohnsdorf contains a layer of clay remarkable for its homogeneous character and great plasticity. The clay bed is nine feet thick. So free is it from foreign bodies that plates of mica are only recognizable with the microscope. It would appear that the only local change that the clay had undergone before deposition was that of elutriation. When analysed it gave these numbers:—

SiO_2.	Al_2O_3.	MgO.	CaO and FeO.	H_2O.	
59·2	14·0	6·2	traces	20·3	= 99·7

The clay belongs to that class of hydrated silicates of alumina and magnesia, which, from being greasy to the touch, are called soapstone; they doubtless derive their origin from serpentine. Similar clays are found in serpentine at Kynance Bay, and Gue Graze, in Cornwall, and contain from 18 to 33 per cent. of magnesia. The Fohnsdorf clay differs from them in containing a much smaller amount of this base.

W. F.

Magnetic Pyrites, from New York. By H. C. Hahn.‡

This specimen of pyrites gave on analysis, after deducting the apatite and hornblende disseminated through it, the following numbers:—

58·31 per cent. iron, 2·28 nickel and cobalt, and 39·41 sulphur.

The composition indicates the formula $6FeS + FeS_2$ or $5FeS + Fe_2S_3$, in which a portion of the iron is replaced by nickel and cobalt.

W. F.

* Jahrbuch für Mineralogie, &c., 1871, 175.
† Jahrbuch für Mineralogie, &c., 1871, 176.
‡ Jahrbuch für Mineralogie, 1871, 177.

Sandbergerite. By A. KENNGOTT.*

THE author had already shown that analyses of the fahlore group were deserving of special attention for the light they throw on the constitution of this mineral; those of sandbergerite also call for remark. Mercier found in it 41·08 per cent. copper, 2·77 lead, 7·19 zinc, 2·38 iron, 7·19 antimony, 14·75 arsenic, and 25·12 sulphur. Or by calculation—

1·967 arsenic	6·469 copper	1·106 zinc	7·850 sulphur
0·589 antimony		0·425 iron	
		0·134 lead	
2·556		1·665	

The metals require as 1·278 R_2S_3, 3·234 Cu_2S, and 1·665 RS, 8·733 sulphur, 3 per cent. too little sulphur was therefore found. Apart from this, calculation gives for $1R_2S_3$,2·53Cu_2S,1·30RS, hence we may have no hesitation in finding the ratios corresponding to the formula of fahlore, which, as 1RS requires 1·95 Cu_2S, will here be—

$$2(4Cu_2S,R_2S_3) + (4RS,R_2S_3),$$

if Cu_2S be not added to RS.

W. F.

Remarkable Concretions of Chalcedony from Brazil. By H. ROSENBUSCH.†

IN the valley of the Jahu, a tributary of the Tiété, on the table land of S. Paulo, the author found, in a bed of marl, chalcedony in the form of long cylindrical tubes, some of them 50 mm. long and from 5 to 8 mm. in diameter. They are for the most part well rounded and hollow; the interior is coated with red ochre which contains much organic matter, a tube when heated emitting a strong empyreumatic odour. Some of the flattened tubes are clearly formed by the union of several smaller ones. In a microscopic section of a tube perpendicular to its axis, a fibrous structure is observed, the fibres being uniformly radii; that cut parallel to the axis is finely granular. The tube is coated on the outside with a crust of quartz crystals, that are in their turn covered with chalcedony, and on which finally, and lying in contact with the marl, is another layer of quartz. These crystals exhibit the one rhombohedron only, the other is altogether absent or but slightly apparent. Other quartz concretions from this region are much contorted, many having dendritic forms. That these remarkable structures have an

* Jahrbuch für Mineralogie, &c., 1871, 179.
† Jahrbuch für Mineralogie, &c., 1871, 175.

organic origin can scarcely be doubted. They strikingly recall the indusial limestone of Auvergne.

W. F.

A Remarkable Well. By H. VOGELSANG.*

IN the months of August and September last, a strange phenomenon was witnessed at Delft during the operation of boring for water. Like appearances had hitherto been remarked in hot springs only, and have consequently been ascribed to the agency of heat.†

On the 3rd August the iron tubes of a Norton's well had been driven to a depth of about 17·5 metres, when of a sudden there was a rush of gas up the tube followed immediately by a jet of water, which was driven with such violence against the monkey as to slightly lift it; on removing it, a foaming column of water and gas rose 14 metres high in the air, and played without intermission for 14 hours, when it ceased to be continuous, and appeared after intervals of 9 minutes. The discharge of gas always increased after such an interval of rest; at first the water poured quietly out over the top of the tube, then rose, till, foaming with gas, it reached a height of 8 metres; soon fell again, and in about a minute was still. The gas readily ignited, burning with a large but feebly luminous flame.

This intermittent activity lasted till the 21st August, the intervals of rest gradually lengthening, and terminating with an evolution of gas alone. The tube was driven further; at a depth of 25 metres sand and water were pumped out; and at 30 metres the desired supply of water was reached.

The water in the earliest stage of the eruption contained much iron, probably in the form of carbonate; its temperature throughout the period of observation was 13° C. The gas collected during three days had the specific gravity and composition by volume given below:

Date.	Specific gravity.	Composition.	
		CO_2.	CH_4.
6th August.....	0·716	16·4	83·6
10th ,, ...	0·754	20·3	79·7
16th ,, ...	0·669	11·6	88·4

Carbonic oxide and heavy hydrocarbons were not present.

The surrounding ground consists of beds of alluvium to a great

* Pogg. Ann., cxlii, 268.

† There is a gas well at West Bloomfield, county of Ontario, State of New York, of which a description will be found in Sill. Amer. Journal for 1870, 336. Gas alone flows from this well, and it has maintained its activity for four years. In a still atmosphere the flame is 30 feet high. The temperature of the gas is probably 10° C.; it consisted of 82·41 CH_4, 10·21 CO_2, 4·31 N, 0·23 O, and 2·94, illuminating hydrocarbons absorbable by Nordhausen acid.—W. F.

depth. The author maintains that the lower end of the tube, after traversing the alluvium and a bed of clay below it, entered one of peat, where by the action of water on its organic remains the gases had been generated and stored up.

W. F.

The Franklin Meteorite. By G. Brush.*

This stone fell four miles from Frankfort, in Franklin county, Alabama, on the 5th December, 1868. It weighed 1 lb. $9\frac{1}{2}$ oz., and has a mean specific gravity = 3·31. It contains—

SiO_2.	Al_2O_3.	Iron oxide.	Chromium oxide.	MgO.	CaO.	K_2O.	Na_2O.	S.	
51·33	8·05	13·70	0·42	17·59	7·03	0·22	0·45	0·23	= 98·02

with a trace of nickeliferous iron.

The chromium oxide corresponds to 0·62 per cent. chromite, the sulphur to 0·63 per cent. troilite. This stone belongs to the class to which G. Rose has given the name of howardite, and resembles in its physical character the meteorite of Petersburg, Tennessee.

W. F.

The Wisconsin Meteoric Iron. By L. Smith.†

At Trenton, Washington county, Wisconsin, several masses of meteoric iron have been discovered. The largest was 14 inches long, 8 inches broad, and 4 thick, and weighed 62 lbs. Its specific gravity is 7·82, and its composition—

Fe.	Ni.	Co.	P.	Cu.	Insoluble.	
91·03	7·20	0·53	0·14	trace	0·45	= 99·35

W. F.

The Black Colouring Matter of Tadjérite. By S. Meunier.‡

Those classes of meteorites, to which the author has given the names of aumalite, chantonnite, lucéite, montréjite, &c., undergo an entire change by exposure to a red heat for a few minutes. From their normal grey colour they turn black, and become at the same time more compact, tough, and dense, and are no longer to be distinguished from tadjérite, a name assigned by M. Meunier to the rock composing the meteorite which fell at Tadjéra, near Setif, on the 9th of June, 1867.

It seemed at first sight probable that the black hue arose from a par-

* Jahrbuch für Mineralogie, &c., 1871, 178.

† Jahrbuch für Mineralogie, &c., 1871, 178.

‡ Comptes rendus, lxii, 393.

tial oxidation of the iron. But the tint was developed in the Setif stone before it reached our atmosphere, is also to be observed in the fragments enclosed in the Deesa iron, and can readily be produced in the absence of every oxidizing agent. A fragment of a Pultusk stone became black when heated in carbonic acid, and, conversely, a splinter of the Setif meteorite neither lost colour, nor became paler when heated in hydrogen. Calcined in excess of air the product is no longer black but of an ochrey red, and fragments heated in a crucible, though remaining black within, take on the surface a reddish colour. The dark hue of montréjite, after the operation, gives it a resemblance to stauropolite. Nothing is evolved by the stone during calcination, and its weight is unchanged.

The metamorphosis which the stone undergoes is in fact a molecular change, and is in no wise due to the taking up or removal of particular elements; this indeed is shown by microscopic examination. The black substance is very far from forming the mass of the stone, and many parts will be seen where it is not to be recognized. These are colourless and highly crystalline, while the dark portion is opaque, has apparently no definite structure, and is irregularly disposed throughout the stone. The grey meteorites which thus change colour by heat are, in the author's opinion, composed of ferro-magnesian silicates, which appear to split up during calcination into a colourless magnesian silicate and a black silicate of iron.

The latter substance is attacked by acid, even in the cold. A portion of a Pultusk stone, calcined, powdered, and treated with hydrochloric acid had, after the lapse of a month, lost its colour and resembled in all respects the original material.

The black portion of the Setif stone has been shown (*Comptes rendus*, lxvi, 514) to be attackable by acid, and to have the composition of peridot.

The granules of the Montréjeau meteorite, composed, according to Damour (*Comptes rendus*, xlix, 31), of felspar and pyroxene, likewise became completely black. Though insoluble before calcination, they are acted on by acids after this operation, and again lose their black colour. This change, possibly a kind of liquation, may explain the partial solubility in acid of certain silicates after they have been subjected to a high temperature; and it is not improbable that the colour of certain black serpentines may be due to a like cause.

W. F.

Organic Chemistry.

On Structural Formulæ and the Theory of the Linking of Atoms. By H. KOLBE.*

IN this paper the author states his objections to the now generally received structural formulæ, founded on the hypothesis of the linking together of similar atoms, and proposes in particular a formula for quinone, $C_6H_4O_2$, which does not involve the assumption that the two oxygen-atoms are linked together by one of their units of affinity, so as to form a bivalent group.

On the Dehydration and its importance to Vegetable Life and to Fermentation. By ADOLF BAEYER.†

IN the investigation of those bodies which are built up of carbon, hydrogen, and oxygen, the separation of water plays as important a part as oxidation and reduction. Nevertheless, this subject has hitherto never been treated with that generality which it deserves; the author has therefore given a connected sketch of the most important reactions depending on the abstraction of water.

In the first place, all oxygen compounds may be derived from hydroxyl-substitution products. Leaving out of consideration the peroxides and quinones, oxygen in C, H, O compounds can occur only in three forms, viz., as C—OH, as C—O—C, or as C=O. The combination C—O—C corresponds to the ethers and anhydrides, and may be converted, as a rule, by absorption of water into 2(C—OH). The C=O group is met with in the aldehydes, ketones and acids, and, as a rule, cannot be converted into the $C\begin{smallmatrix}OH\\OH\end{smallmatrix}$ group, since this group in most cases passes spontaneously into C=O. In glyoxylic and mesoxalic acids, and chloral hydrate, both forms are known, and may be readily converted one into the other. In the case of the ordinary aldehydes, ketones and acids, on the other hand, only the ethers are known, tribasic formic ether, for example. The conditions which determine the stability of the $C\begin{smallmatrix}OH\\OH\end{smallmatrix}$ group have not yet been fixed, but it would seem that the presence of negative elements, such as O and Cl, is favourable to it. For instance, mesoxalic ether, according to Deichsel's experiments, is—

$$C_2H_5O.CO.C(OH)_2.CO.OC_2H_5.$$

and cannot be rendered anhydrous without decomposition. Again chloral combines readily with water, forming chloralhydrate $CCl_3.CH$

* J. pr. Chem. [2], iii, 122.

† Chem. Centralblt., 1871, 27—38, from Deut. Chem. Ges. Ber., iii, 63.

$(OH)_2$, whereas aldehyde does not. Corresponding to chloralhydrate is the sulphur compound $CH_3.CH(SH)_2$, obtained by the action of H_2S on aldehyde, which is converted into sulphaldehyde $CH_3.CHS$, in presence of hydrochloric acid. Ammonia, on the other hand, destroys the stability of the $C(OH)_2$ group; ammonium glyoxylate and mesoxalate, and alloxan, the ureide of mesoxalic acid, contain only CO, ammonium mesoxalate dried *in vacuo* being $NH_4.O.CO.CO.CO.ONH_4$.

The problem of the abstraction of water comprises two propositions, namely to determine the position occupied by the elements of the escaping water, and secondly, to ascertain the fate, so to speak, of the affinities thus set free. If the one limiting condition be assumed, that in the formation of water, an O-atom does not quit the H-atom with which it is already united, then in the case of the hydroxyl-substitution products, the formation of water can take place in two ways only, OH combining either with an H-atom which is united to O, or with an H-atom which is united to C.

After the separation of water, two units of affinities remain unsaturated. If these two mutually satisfy each other, and this is the most usual, and may be considered the normal course, there is then, in the first case, of the two OH groups one O left, which either connects two C-atoms, or remains wholly combined with one. This reaction is termed *the formation of anhydrides*, and its result is either the group C—O—C or CO. In the second case, by the union of OH with an H-atom united to C, two C-affinities become free, whereby the two C-atoms become united by one affinity of each, if not previously combined, by two of each if previously simply combined. This may be termed *condensation.*

Normal condensation is, however, not a necessary consequence of the separation of water in the form of OH and H united to C; the C-affinities may also remain unsaturated, or combine in an order different from that which corresponds to the separation of OH and H. Reactions in accordance with the latter rule seem to be rare; in fact the author believes no such to have been established. The same holds good for the separation of water in the form of OH and H united to O. Finally, as will be shown in the third section, the free affinities can take up water or some group derived therefrom.

The *formation of anhydrides*, and *condensation*, may be divided, according to the position of the water-forming elements, into internal and external: that is to say, into those in which the process takes place within the molecule, and into those in which it takes place between two separate molecules. The internal may be subdivided into three groups, according as it takes place on the same carbon-atom, on two adjacent, or on non-adjacent carbon-atoms.

I. *Formation of Anhydrides.*

(a.) *Simple:* 1. *Internal formation of anhydrides on the same C-atom.* Formation of the aldehydes, ketones, and acids from the normal hydrates, *e.g.*, $CH(OH)_3 = CHO.OH + H_2O$: formic acid.

2. *Adjacent.* Ethylene oxide from glycol—

$$CH_2(OH).CH_2)(OH) = \underset{\diagdown\ \diagup}{CH_2\ CH_2}\text{; Epichlorhydrin.}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad O$$

3. *Non-adjacent.* Anhydrides of bibasic acids—

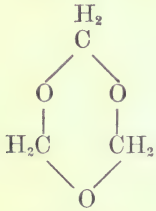
$$\text{Coumarin, } C_6H_4 = \begin{matrix} CH.CHCO \\ O\text{———}\end{matrix}\!\!>\text{;}$$

4. *External formation of anhydrides.* Ethers, anhydrides of the acids, &c.

(b.) *Compound.* The same process may take place from one to four times on the same C-atom, *e.g.*, Basset's orthocarbonic ether, tribasic formic ether, aceticaldehyde. The polymeric aldehydes probably belong also to this class—

$$C\left\{\begin{matrix} H_3 \\ OCH_3 \end{matrix}\right. \qquad C\left\{\begin{matrix} H_2 \\ (OC_2H_3O)_2 \end{matrix}\right. \qquad C\left\{\begin{matrix} H \\ (OC_2H_5)_3 \end{matrix}\right. \quad C(OC_2H_5)_4.$$

Methylic ether. Acetic aldehyde. Tribasic Formic ether. Orthocarbonic ether.



Dioxymethylene.

II. *Condensation.*

(a.) *Simple.* 1. *Internal on the same C-atom.* The formation of carbonic oxide from formic acid is an instance of separation of water in accordance with this reaction. No condensation here takes place, as is well known; the C-affinities remain unsatisfied. This reaction has not yet been shown to occur in any other case.

2. *Internal condensation on adjacent C-atoms.* This takes place in the formation of ethylene and its homologues from the corresponding alcohols—

$$CH_3CHHCH_2(OH) = CH_3CH{=}CH_2.$$

Propylic alcohol. Propylene.

The result is, that the C-atoms, previously simply combined, become united by two affinities of each.

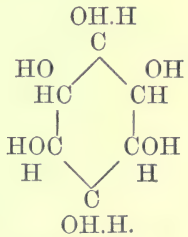
3. *Between non-adjacent C-atoms.* Unknown.

4. *External condensation.* This reaction consists in the union of OH of one molecule with H of another molecule to form water, the two molecules then uniting by their free affinities. This happens in the formation of sulpho-acids: $C_6H_6 + SO_2(OH)_2 = C_6H_5.SO_2.OH$. With mere carbon-compounds, it seems rarely to occur, if, as is the case in this paper, we consider only those reactions which are effected by simple abstraction of water without the influence of other agents. A process of great importance evidently belongs here, viz., the formation of methylenitan from formic aldehyde. Butlerow has shown that a saccharine body is formed when an aqueous solution of formic aldehyde is treated with alkalies. In the gaseous state, formic aldehyde has the composition CH_2O, according to Hofmann's experiments, but nothing prevents us from considering it as $CH_2(OH)_2$ when in aqueous solution. If it be now assumed that one OH in each molecule forms water with one H of the other molecule, and that the C-affinities thus set free unite, then, taking 6 molecules, the following equation is obtained:—

$$6CH_2(OH)_2 - 5H_2O = C(OH)_2H.C(OH)H.C(OH)H.C(OH)H.C(OH)H.C(OH)H_2.$$

If a further molecule of water be then removed from the $C(OH)_2H$ group on the left, or if by condensation between the two end-terms a ring is formed, there is obtained either—

$$COH.[C(OH)H]_4.CH_2(OH),$$ or,



Carius's phenose.

If the condensation of three molecules only takes place, then propylphycite, the aldehyde of glyceric acid, is formed—

$$3CH_2(OH)_2 - 2H_2O = C(OH)_2H.CH(OH).CH_2(OH).$$

According to our present knowledge, the composition of grape-sugar must correspond with one or the other of the above formulæ, or it is at least very closely related to them, and, therefore, it is highly probable

that the formation of sugar in the plant is in close connection with the reaction above discussed. The general theory of the formation of sugar and allied substances in the plant is that the carbonic acid is reduced in the green parts by the action of light, and is converted by gradual synthesis into sugar. The intermediate terms have been sought in the organic acids—formic, oxalic, tartaric acids—which certainly may be looked upon as reduction-products of carbonic acid. According to this view, then, at those moments when the plant reduces most powerfully, that is by the action of the sun's rays on the green portions of the leaf, there is produced a great accumulation of acids which can be only gradually replaced by sugar. This has hitherto never been observed; and when it is considered that under all circumstances sugar and its anhydrides are formed in the plant, but that the acids are found in different species in different parts, and again vary with the age of the plant, the often-expressed theory that the sugar is directly derived from the carbonic acid becomes more probable. Butlerow's discovery is the key to this. The similarity existing between the colouring matter of blood and the chlorophyll of plants has often been pointed to. It must, therefore, also appear probable that chlorophyll fixes carbonic oxide just as hæmoglobin does. When sunlight falls upon chlorophyll which is surrounded by CO_2, the carbonic anhydride seems to suffer the same dissociation as at high temperatures, O being liberated and CO remaining combined with the chlorophyll. The simplest reduction of carbonic oxide is to formic aldehyde; it need only take up hydrogen, $CO + H_2 = COH_2$; and under the influence of the cell-contents, just as by the action of alkalies, this aldehyde is transformed into sugar. Glycerin might be formed by the condensation of three molecules and reduction of the glyceric aldehyde. The formation of sugar in some other less simple way is, however, not excluded by this, and it is very possible that under certain circumstances the vegetable acids may be converted into this substance which, in a thousand varying forms, helps to build up the structure of the plant.

In what manner the cell-contents cause the condensation of the formic aldehyde cannot for the present be ascertained, nevertheless it is probable that in the first instance the sugar formed combines with it, and is afterwards, according to circumstances, split off as cellulose, starch, or glucosides.

(b.) *Compound: 5. Bivalent external condensation.*

On the separation of water according to the preceding rule, carbon atoms before uncombined become united by one affinity of each. According to the second rule, C-atoms already simply combined become united by two affinities of each. If both these reactions occur simultaneously, a condensation takes place, such as is exhibited by the aldehydes and ketones, and consists in the combination of the oxygen

of the CO group with 2H of the methyl group, the two C-atoms then uniting by two affinities of each. This may be termed *carbonyl-methyl-condensation*, and the name *hydroxyl-hydrogen-condensation* may be applied to simple condensation.

The condensation of the aldehydes and ketones which belongs to this class, the formation of cinnamic acid, of mesityl oxide, and of phorone, were discussed by the author on a former occasion.* Two fresh instances have since been discovered, viz., the synthesis of coumarin from salicylic aldehyde and acetic anhydride by Perkin, and Kekulé's discovery of crotonic aldehyde. Both of these confirm the author's previous views, and he further remarks that Kekulé's views on condensation and the formulæ of mesityl oxide and phorone, are entirely in accordance with his own.

Condensations corresponding to this rule are induced even in the cold by the most varied agents, and, therefore, no doubt, play just as important a part in the vegetable kingdom as does simple condensation. Indeed this thought, which first led the author to the study of these reactions, was constantly sustained by the various plant-odours of peppermint, camphor, orange, and turpentine oil, met with in the course of the investigation. Unfortunately, however, he was never successful in obtaining a body actually occurring in the vegetable kingdom.

6. *Bivalent internal condensation on non-adjacent C-atoms:* mesitylene from phorone.

7. *The same on adjacent C-atoms:* the formation of acetylene from glycol, or aldehyde, would be an instance of this, if observed.

The author holds it to be unnecessary to consider all other possible cases and their modifications, since they may be all referred, as those already treated or considered, to the two typical forms of anhydride-formation and condensation. He brings forward one other group of phenomena in which a movement and alteration of position of the oxygen-atoms takes place, and, on account of fermentation probably being comprised in them, he terms these reactions fermentation-phenomena.

III. *Fermentation Phenomena.*

According to Strecker, paralactic acid (Fleischmilchsäure) when heated to 130°, is converted into the anhydride of ordinary lactic acid. Further, it has been shown by Dosios that paralactic acid yields malonic acid by oxidation, so that on heating it a movement of the oxygen from one C-atom to the other takes place.

$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.CO.OH \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ CH.OH.CO.OH. \end{array}$$

Paralactic acid. Lactic acid.

* Ann. Ch. Pharm., cxl, 306, and Suppl. Bd., v, 79.

Wurtz found that when glycol is heated with zinc chloride, aldehyde and its products of condensation are formed, and not ethylene oxide, as might be expected.

This has been confirmed by Bauer:

$CH_2.OH$	CH_3	CH_3
|	|	|
$CH_2.OH$	$CH(OH)_2$	$CH.O$
Glycol.	Aldehyde-hydrate.	Aldehyde.

Again, Carius has found that aldehyde is formed on heating ethylene bromide with water. It is not necessary in this case to assume a re-arrangement of the bromine, but it may be conceived that glycol is formed in the first instance, and, in accordance with Wurtz's reaction, passes into aldehyde.

Glycerin, when heated with acid potassium sulphate, yields acrolein. On the one side simple condensation takes place; on the other the same movement of O, as in the case of glycol:

$CH_2.OH$	CH_2	CH_2
|	||	||
$CH.OH$	CH	CH
|	|	|
$CH_2.OH$	$CH.(OH)_2$	$CH.O$
Glycerin.	Acrolein-hydrate.	Acrolein.

All these reactions have this feature in common, that they take place at high temperatures, and in the presence of water-withdrawing agents. In every case the result is the same when the hydrate formulæ are compared: the OH groups quit their position and pass to another C-atom, which is already united with an OH or carboxyl group. We certainly do not go wrong in assuming that, under these circumstances, the reason of the movement and change of position of the oxygen lies in the separation of water, and it only remains to investigate why such remarkable consequences follow on this.

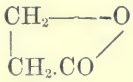
If the passage of glycol into aldehyde be considered, the following possibilities suggest themselves:—

1. Two molecules mutually interchange OH and H. This reaction is without analogy.

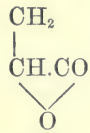
2. The oxygen of the one hydroxyl quits its H and combines with the H of the other hydroxyl, and with an H united to C. This is also highly improbable.

3. Anhydride formation takes place between the two OH groups, and re-arrangement of the ethylene oxide formed ensues. The behaviour of paralactic acid seems to be in favour of this view, as it can be so explained, that the carboxyl forms an internal anhydride with

the OH, and then in a certain measure attracts the O to its own carbon-atom:



Paralactic anhydride.



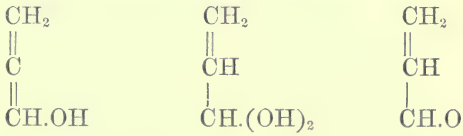
Lactide.

In that case, however, lactide would be formed, whereas Strecker obtained only dilactic acid.

4. The one hydroxyl forms water with an H of the other C, as in the formation of ethylene, and vinylic alcohol results, which by re-arrangement passes into aldehyde. This view is admissible in the case of the aldehydes, but not in that of lactic acid, which would yield acrylic acid, not convertible by re-arrangement into lactic acid.

5. The same as in 4, but after the separation of water, a molecule of water is absorbed again, but in different order.

Of all the instances enumerated, the fifth is the most probable, because the same reaction is observed by the monhydric alcohols. For instance, when propylic alcohol is deprived of water, propylene is formed, which, under the influence of concentrated sulphuric acid, again absorbs water, and is converted into isopropylic alcohol. Here, then, is a similar movement and alteration of position of the oxygen, and it is only necessary further to assume that in the case of vinylic alcohol the absorption takes place spontaneously, and without help of an intermediary, because an OH is already present in the ethylene. According to this the formation of acrolein might be explained as follows:



In the first place 2 mols. OH_2 are separated from glycerin, and an alcohol is formed, which by absorbing water, is converted into acrolein hydrate, and this on the loss of OH_2 passes into acrolein.

In the case of paralactic acid, acrylic acid would be formed, and this by absorbing water passes into lactic acid. Or, what is still more probable, the carboxyl of a second molecule of lactic acid combines with the acrylic acid, just as sulphuric acid combines with ethylene, forming the mixed anhydride.

The improbability of water being at the same time separated, absorbed, and again separated, cannot well be urged as an objection against these reactions. Sulphuric acid exhibits a precisely similar

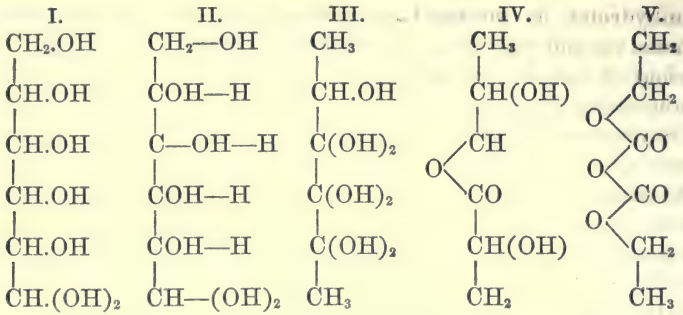
behaviour in the formation of ether, when under the same conditions it combines with alcohol, is separated from it, and again combines.

A dihydric and a trihydric alcohol behave similarly; one molecule of OH_2 is separated and one is re-absorbed, but is differently distributed in the molecule, so that the OH group passes to the same C-atom on which another is already situated; the result is the formation of the aldehyde group, one portion of the alcohol being reduced, the other oxidised.

It is usual to extend all that is said of alcohol, glycol, and glycerin as a matter of course to sugar. Following this custom, a series of remarkable, as yet unexplained reactions is met with, which certainly belong to this category, viz., the phenomena of fermentation. The result of alcoholic and lactic fermentation is, exactly as in the formation of acrolein and aldehyde, the reduction of one part and the oxidation of the other. In fact this process may be similarly interpreted by alternate absorption and separation of water.

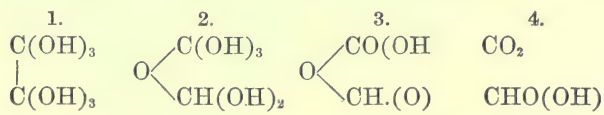
The products of the separation of water from the sugars may be divided into two classes, the one comprising the anhydrides which occur in the plant, the other those artificially obtained. The former, on account of the ease with which they may be split up, have always been looked upon as ethers; of the nature of the latter, *e.g.*, caramel, glycinic acid, so much only is known that they cannot be reconverted into sugar, and have therefore probably undergone a more profound change. The formation of caramel precedes that of glycosan and lævulosan, which are convertible into sugar by absorption of water, but cannot be fermented. This might be urged against the view that fermentation is a consequence of the separation of water. Too great weight, however, cannot be laid on this point, when it is considered in what various ways sugar can give up water.

The representation of the process of fermentation by a chemical formula is rendered difficult by the fact that the constitution of the sugars is still but imperfectly known. The conversion of mannite into hexylene, and of milk sugar into adipic acid proves that the hydrocarbon from which they are derived is a normal one; but it is not known in what respect the sugars which contain 2H less than mannite differ from this latter. The formation of sugar from formic aldehyde, and the formulæ of mucic and saccharic acids, render it probable that sugar is a kind of propylphycite, *i.e.*, an aldehyde. The following formulæ, in which, for the sake of clearness, one molecule of water has been added to sugar, represent the reactions which take place in lactic and in alcoholic fermentation:—



The first formula is that of the unchanged sugar; in the second the elements of the separating water are indicated by short lines placed before them; in the third as much water has been absorbed as was separated, but OH and H are differently distributed in the molecule. It is not necessary to assume here that the compound which results on the separation of water, as in II, contains at any moment C-atoms united by two affinities of each; there is no difficulty in conceiving that the resulting skeleton immediately combines *in statu nascendi* with water, forming the group represented in III. In the third formula, the whole of the oxygen is collected at one point in the molecule, a phenomenon which may be termed *accumulation.* The consequence of the accumulation of oxygen is the fracture of the carbon chain, which in lactic fermentation occurs once, in alcoholic thrice. This fracture is universally observed wherever a similar accumulation of oxygen takes place.

If, for instance, the decomposition of oxalic acid into formic acid and carbonic anhydride on heating with glycerin be considered as it is represented by the following formulæ, it will be seen that on the breaking up of the molecule, the atoms of the one OH group become so distributed that whilst the H passes to the other C-atom, the O forms a connecting link between the two carbons.



1. Hypothetical hydrate of oxalic acid. 2. Isomeric fractured molecule. 3. Anhydride of formic and carbonic acids. 4. Carbonic anhydride and formic acid.

This behaviour of oxalic acid also explains the partial reduction which the sugar molecule, as represented in III, undergoes on fracture.

Formulæ IV and V, which correspond to the third oxalic acid formula, represent the anhydrides of lactic and ethylcarbonic acids as the product of fermentation. Although it is not necessary to assume

the anhydrides as intermediate products, the connection between accumulation and fracture is rendered more evident by so doing. The behaviour of liquids fermented under pressure is also in favour of the assumption that these anhydrides are the primary products of fermentation, Stahlschmidt having observed that champagne contains ethylcarbonic acid. The formation of succinic acid and other bye-products may be explained in the same way as the main reaction: in some molecules the accumulation, and consequently the fracture, takes place at a different part of the carbon chain.

It is assumed in the above that the molecules of sugar which undergo fermentation do not take part in the nourishment of the yeast plant, but simply receive an impetus from the same, which may be compared to the action of heat and of water-withdrawing agents. Liebig's latest researches on fermentation confirm these assumptions, and afford at the same time a further proof of the correctness of the above enunciated views on the chemical nature of fermentation.

H. E. A.

On the Action of Liquid Phosgene on some Organic Compounds. By T. Kempf.*

The previous experiments† of the author are here completed. A mixture of phenol (3 parts) and liquid phosgene (2 parts) was heated for several hours in sealed tubes, and then submitted to distillation, but the author did not succeed in isolating the chlorinated compound $C_6H_5O.COCl$; evidence, however, of its existence was furnished by dissolving the distillate in dry ether, and saturating it with gaseous ammonia. After separating the ammonium chloride from the solution, it gave on evaporation fine plates of phenyl carbamate, $CO\left\{\begin{matrix} HN_2 \\ OC_6H_5 \end{matrix}\right.$. It melts at 141°, is soluble in alcohol and ether, with difficulty in cold water, but more readily in hot. Treated with caustic soda it yields ammonia, sodium carbonate, and sodium phenylate. With ammonia solution at 140° phenol and urea.

The residue of the distillation, as also the solid substance obtained by treating the contents of the tubes with dilute soda solution, is phenyl carbonate. The author succeeded in nitrating the phenyl carbonate by covering a mixture of nitric and sulphuric acid with a layer of nitric acid, and then gently adding the carbonate. In the course of a few days it formed a homogeneous mixture, from which water threw down pale yellow flocks. These, when washed and crystallised from benzol, gave yellow crystalline nodules of dinitrophenol

* Zeitschr. f. Chem. [2], 77—79, from J. pr. Chem. [2], i, 402.

† Zeitschr. f. Chem. [2], vi, 205 and 235.

carbonate $\begin{matrix} C_6H_3(NO_2)_2 \\ C_6H_3(NO_2)_2 \end{matrix} \left\{ \begin{matrix} O \\ O \end{matrix} \right\} CO$. This compound melts at 125·5°, and when slowly heated gives off irritating vapours; heated quickly it explodes. It is but slightly soluble in water, alcohol, or ether. By long continued boiling with water or dilute alcohol, it is decomposed into carbonic anhydride and dinitrophenol, as also when heated with water in a sealed tube. Heated with caustic baryta, it yields barium carbonate and barium dinitrophenylate.

Cresol behaves with liquid phosgene in a manner similar to phenol. The author did not succeed in isolating the cresyl chlorocarbonate, but by treatment with ammonia, cresyl carbamate $CO \left\{ \begin{matrix} H_2N \\ OC_7H_7 \end{matrix} \right.$ was obtained. It melts at 125°, is only slightly soluble in cold water, but readily in hot water, alcohol, and ether. The author did not obtain the cresyl carbonate.

Thymol is acted on by phosgene with much greater difficulty than phenol and cresol, but the author succeeded in preparing the compounds corresponding to those above described.

Action of Phosgene on Benzoyl Hydride.—Benzoyl hydride and phosgene when heated to 120°—130°, gave off much carbonic anhydride, and the product after agitation with acid sodium sulphite to remove the undecomposed aldehyde, was treated with water, when a heavy oil remained undissolved. This when purified by distillation was analysed and found to be benzyl chloride $C_6H_5.CCl_2H$. Its formation is represented by the equation: $C_6H_5.COH + COCl_2 = C_6H_5.CCl_2H + CO_2$.

Action of Liquid Phosgene on Acetic Acid.—These substances react on one another at 110°—120°, yielding acetyl chloride: $CH_3.CO.OH + COCl_2 = CH_3.CO.Cl + HCl + CO_2$.

Acetone and phosgene heated to 110°—120° for some days gave but a very small quantity of a liquid boiling at 120°—135°, and which the author believes to be dichloracetone. Epichlorhydrin, lactic acid, carbon disulphide and mononitrophenol are scarcely acted upon by liquid phosgene.

C. E. G.

On the Production of the Olefines from Paraffin by Distillation under Pressure. By T. E. Thorpe and John Young.

Paraffin exposed to a high temperature in a closed vessel is completely resolved, with evolution of but little gas, into hydrocarbons, which remain liquid at the ordinary temperature. By this process $3\frac{1}{2}$ kilogrammes of paraffin, melting at 44·5 C. (prepared from shale) yield nearly 4 litres of liquid hydrocarbons. This mixture begins to boil at 18°, and is made up of hydrocarbons, boiling

	Litres.
Between 200° and 300°	2·7
„ 100° „ 200°	1·0
Below 100°	3
	4·0

The portion boiling below 100° is composed mainly of olefines, the proportion of members of the paraffin series, C_nH_{2n+2}, being but small. By repeated fractionation over sodium, perfectly colourless liquids are obtained, boiling at about 35° and 65°, which are attacked by bromine in the cold with the greatest energy. On adding the bromine slowly, and in minute drops, and carefully cooling the hydrocarbon by a mixture of snow and salt, scarcely a trace of hydrobromic acid is produced. The portion boiling at 36° is mainly amylene; it absorbs bromine with the greatest avidity, and is almost wholly converted into amylene bromide, boiling at 184°—188° (Wurtz states that the boiling point of this bromide is about 180°).

Exactly similar results are obtained from the portion boiling at 65° to 70°. This, from its boiling point, may be either C_6H_{12} or C_6H_{14}, or a mixture of both. Bromine disappears instantly on adding it to the carefully cooled liquid, and on distillation by far the greater portion is found to have combined with the halogen. The bromide thus obtained distils with slight decomposition at about 195°. Pelouze and Cahours found that hexylene bromide, $C_6H_{12}Br_2$, boiled at 192° to 198°.

J. B.

Conversion of Formic Acid into Methyl Alcohol. By Ad. Lieben and A. Rossi.*

The authors have extended the general method of preparing ketones to the particular case of formic aldehyde. E. Mulder had already obtained, by heating calcium formate, a distillate which reduced silver oxide, and appeared to have the properties of Hofmann's formic aldehyde. Lieben and Rossi subjected calcium formate to dry distillation in portions of 10 grms., the pyrogenous products being cooled by means of a freezing mixture. From 100 grms. of calcium formate, a very small quantity of liquid distillate was obtained, which had a smell resembling that of aldehyde, and reduced ammoniacal solution of silver oxide. The distillate was mixed with water, and hydrogenised by sodium amalgam and sulphuric acid in equivalent proportions. By this treatment, methyl alcohol was produced, which was separated from the liquid by distillation, and was dehydrated by potassium carbonate and by lime. The conversion of the formic aldehyde into methyl alcohol was not completely effected by repeated treatment with sodium amalgam.

* Ann. Ch. Pharm., clviii, 107—112.

The quantity of methyl alcohol obtained from 250 grams of calcium formate did not amount to more than three or four grams. It boiled at 66°—67°; and gave by heating with fuming hydriodic acid, methyl iodide, which distilled over at 43° to 44°. The methyl iodide was further identified by analysis, and by the formation of the characteristic methyl oxalate, by its action on dry silver oxalate.

W. H. D.

On Sulphocarbonyl chloride and a new Sulphochloride of Carbon, or Perchlormethyl Mercaptan. By B. RATHKE.*

CARBON bisulphide is left for some weeks in contact with manganese peroxide and hydrochloric acid, with frequent agitation, but the time can be considerably shortened by the addition of a small quantity of iodine. On distilling the mixture, a yellow oil first passes over, and is succeeded by a solid substance, Kolbe's trichloromethyl-sulphochloride $CSCl_4O_2$. The whole is then washed, dehydrated by lime, and distilled. The portion boiling below 80° (1) has a reddish yellow colour and a phosphoric odour, and consists of a small quantity of sulphocarbonyl chloride, together with chloride of carbon and unchanged carbon bisulphide; (2) 80°—140° a small quantity of a mixture of 1 and 3; (3) from 140°—150° a considerable quantity of a yellow oil; (4) Trichloromethyl sulphochloride which remains in the retort saturated with this oil. If iodine has been used in the preparation, it must be separated from 1 and 3 by agitation with mercury. By repeated fractioning of 3, a yellow oil is obtained boiling at 146°—147°, having an odour undistinguishable from that of $CSCl_2$, and occasioning a copious flow of tears. Exposed to moist air, it gives off hydrochloric acid, whilst sulphur is deposited on the sides of the vessel. Its composition is $CSCl_4 = CCl_3.SCl$.

When the *perchloromethyl mercaptan* ($CCl_3.SCl$) is heated to 160° with water in a sealed tube, it is entirely decomposed, with formation of hydrochloric and carbonic acids, and liberation of sulphur: $CSCl_4 + 2H_2O = 4HCl + CO_2 + S$. It dissolves, and undergoes the same decomposition when treated with potash solution. With ammonia the reaction is somewhat similar, but the greater portion of the sulphur is precipitated, and at the same time ammonium sulphocyanate is formed, together with a solid substance containing sulphur and nitrogen, which after the removal of the sulphur by carbon bisulphide, appears as a light yellowish brown powder which is insoluble in any menstruum.

The *sulphocarbonyl chloride* is also destroyed when the fluid (1) containing it is agitated with ammonia; ammonium carbonate, chloride, and sulphocyanate being formed.

* Zeitschr. f. Chem. [2], vii, 50, from Deut. Chem. Ges. Ber., iii, 858.

Nitric acid of sp. gr. 1·2 poured on to perchlormethyl mercaptan, changes it in the course of two or three weeks into a solid white substance, melting at 135°, and having the other properties of trichloromethylsulphochloride, $CCl_3.SO_2.Cl$. In the ordinary process for preparing this latter substance, it is evidently produced by the oxidation of the $CSCl_4$ first formed. Potassium iodide acts rapidly on chlormethylmercaptan even in the cold, with formation of hydriodic acid and liberation of iodine, leaving a small quantity of a tough yellowish white solid substance. When $CSCl_4$ is heated to 200° for some hours, it is decomposed, without any alteration in appearance, into chloride of carbon, chloride of sulphur, and a little sulphochloride of carbon. When aniline is added to the mixture (1) of sulphocarbonyl chloride with carbon bisulphide and chloride of carbon, as long as a precipitate of aniline hydrochloride is formed, the solution on evaporation leaves phenyl sulphocyanate: $CSCl_2 + 3NH_2C_6H_5 = 2NH_3C_6H_5Cl + CSN.C_6H_5$. According to Albrecht, when perchlormethyl mercaptan is treated with a concentrated solution of potassium sulphite, it evolves considerable heat, and after a time solidifies to a crystalline pulp, which on recrystallisation yields large crystals of a rather difficultly soluble salt $C(SO_3K)_3.SH$. The free acid from this gives a deep blue colour with ferric chloride, even when very dilute. When the solution of the potassium salt is decomposed by bromine, it is changed into the still more difficultly soluble, finely crystallising compound $C(SO_3K)_3.OH$, sulphuric acid being formed at the same time. The author proposes for these salts the names of *potassium methylmercaptan-trisulphate* and *methylalcohol-trisulphate*.

The action of potassium sulphite on sulphocarbonyl chloride produces the same salt as on the perchlormethyl mercaptan. It is also obtained in small quantity, by digesting carbon bisulphide with dilute alcohol and potassium sulphite. *Chloropicrin* is also easily acted on by potassium sulphite, with formation of a difficultly soluble explosive salt, probably $C(SO_3K)_3.NO_2$. C. E. G.

The Action of Chlorine on Absolute Alcohol. By Ad. Lieben.*

The author finds that the action of chlorine on absolute alcohol always forms chloral alcoholate (melting-point 46°, boiling-point 112°·5—115°), and that the action of sulphuric acid upon this, sets free the chloral. Moreover, the author believes that in the preparation of chloral, ether is formed, and that from this compound, dichlorinated ether is produced, which with alcohol gives ethoxyl-chlorethylic oxide (monochloracetic ether). C. E. G.

* Zeitschr. f. Chem. [2], vii, 58, from Deut. Chem. Ges. Ber., iii, 907.

On the Action of Salts on Alcohol. By K. KRAUT.*

IT has been already shown by the author, that zinc acetate and alcohol readily re-act, with formation of ethyl acetate and zinc hydrate. The present paper consists of an extension of this observation to zinc valerate, and formate, and to various acetates, also to the influence of temperature, duration of heating, &c., on the reaction. Special precautions were taken to obtain the subtances pure and anhydrous.

Zinc acetate acts on alcohol in the absence of water, at ordinary temperatures, but very slowly; on leaving together for $7\frac{1}{2}$ months a mixture of 1 equiv. acetate with 25 equivs. alcohol, about 8 per cent. of the zinc acetate was decomposed. A mixture of 1 equiv. of the acetate with 10 equivs. alcohol, heated for 10 hours to 100°, showed a separation of 64·75 per cent. of the ZnO employed. From a similar mixture heated for 10 hours to 200°—220°, 97·1 per cent. ZnO had separated.

1 equiv. zinc acetate was heated with 10 equivs. alcohol to 100°; there had separated in

5	10	15	30	50 hours.
52·2	64·75	77·4	90·2	93·5 per cent. ZnO.

1 equiv. zinc valerate was heated with 10 equivs. alcohol to 100° for

10	20	30	50 hours.
36·4	61·1	71·2	78·9 } per cent. ZnO
37·8	62·4	71·8	79·6 } separated.

The formation of ethyl formate was observed in the action of alcohol on zinc formate, but the difficulty of drying the zinc salt completely, without some decomposition, rendered it unsuitable for comparative experiments.

Alcohol was found to act on the acetates of ammonium, magnesium, mercurosum, and silver, with formation of ethyl acetate. At 100°, it had no action on sodium acetate.

W. H. D.

On the Boiling point and Atomic Volume of Allyl Alcohol. By B. TOLLENS.†

FOR determining these points, Tollens prepared pure allyl alcohol, which was carefully dehydrated by lime. It then boiled at 96°—97°; a somewhat higher temperature than that previously observed. Its specific gravity was taken at eight different points, progressing from 0° to 93·5°; correction being made for the expansion of the glass of the

* Ann. Ch. Pharm., 323—326.

† Ann. Ch. Pharm., clviii, 104—106.

vessel employed. At 0° specific gravity = 0·8709; at 13° = 0·86045; at 93·5° = 0·78832. The specific gravity of allyl alcohol at 97° its boiling point, compared with that of water at 0° = 0·7846. The atomic volume then = $\frac{58}{0{\cdot}7846}$ = 73·92, which agrees well with the number 73·8 given by Kopp. The oxygen, therefore, existing in allyl alcohol is present as hydroxyl, and has the value 7·8; while the oxygen in the CO of the isomeric acetone has a value = 12·2.

W. H. D.

Explosion of Nitroglycerin. By E. von Gorup-Bezanez.*

The very dangerous nature of nitroglycerin is well known, but it is nowhere stated that under certain conditions even very small quantities may produce such effects more dangerous and terrible even than those of chloride of nitrogen. The author therefore publishes the following as a caution:—

One of the students in his laboratory had prepared a small quantity of nitroglycerin, and was studying its properties. He found, as it is stated, that a thin layer of it burns only with difficulty, and partially like gunpowder. If a little is gently heated in a porcelain dish, and touched with a burning match, it burns with a crackling noise. The student now became confident, and placed about ten drops in a small wrought iron sand-bath, and heated it with a large gas-burner as quickly as possible. First a crackling noise was heard, but a moment afterwards a most terrible explosion took place. All the 46 window-panes of the closed working place were so completely shattered that hardly a piece bigger than a pea could be found; the iron sand-bath was rent in two, one piece being shot through the window of an adjoining working place, and the other quite coiled up. The strong iron retort stand remained standing, but was bent at a right angle, and half of it clean cut through; the upper part of the gas-burner was rent, and the edges jagged.

The conditions under which this explosion took place were similar to those described by E. Kopp (Compt. rend. lxiii, 189). When nitroglycerin is dropped on a moderately hot cast-iron plate it volatilizes quietly; if the plate is red hot the drops burn without noise, like a grain of gunpowder, but if it is not red hot, but hot enough to heat the nitroglycerin to its boiling point, the nitroglycerin decomposes with explosion.

C. S.

* Ann. Ch. Pharm., clvii, 289.

On Inuloïd, a Soluble Modification of Inulin. By O. Popp.*

The expressed juice of the bulbs of the Jerusalem artichoke (*Helianthus tuberosus*) or dahlia, gathered before they are ripe, or rather at the time when the deposit of inulin in the cells first commences, after treatment with lead acetate, gives on standing, a precipitate resembling starch, and having the composition and most of the properties of inulin, but possessing a lower specific gravity, and a higher degree of solubility. Dried over sulphuric acid it has the composition $C_6H_{10}O_5 + H_2O$; at 105° it loses its water; it melts at 130°—135°, passing into an easily soluble state; above this point it decomposes. It has the same rotatory power as inulin; after inversion by acids, $\alpha = -79°$. 100 pts. water at 18°—20° dissolve 1·895 p. inuloïd, and 0·985 p. inulin. It dissolves in an ammoniacal solution of copper sulphate, and on boiling is precipitated as a bluish-green substance, $C_6H_{10}O_5.CuO$, which by protracted boiling divides into inuloïd and copper oxide. It does not reduce alkaline copper tartrate. After some time boiling in water, it passes into a soluble gummy mass; by very long heating with water, or more easily with dilute acids at 110°—120°, it passes into lævulose; with cold concentrated sulphuric acid it forms a conjugate acid, which divides again on dilution; it precipitates metal from hot ammoniacal copper or silver solutions; is not coloured by aqueous solution of iodine or bromine; is not precipitated by aqueous solutions of lead acetate or barium hydrate; but with the latter reagent the addition of alcohol to both solutions before mixing produces a precipitate of $C_6H_{10}O_5.BaO$.

The author considers that in the plant-juice the inuloïd exists in a soluble combination with synanthrose. By treatment with lead acetate, a compound of lead and synanthrose is formed, and the inuloïd is liberated; or this latter may be set free by causing the juice to ferment at 10°—12°, by which means the synanthrose is decomposed.

F. H. H.

On Synanthrose, a new Carbo-hydrate contained in the Synanthereæ. By O. Popp.†

Synanthrose is a variety of sugar which always accompanies inulin in the tuber-bearing compositæ; it occurs in all stages of growth, but most abundantly in the ripe bulbs. *Dahlia variabilis* yields it in the greatest quantity and purest state; but the tubers of *Helianthus tuberosus* may be advantageously used for its preparation. The freshly expressed juice is treated with lead acetate; the excess of lead removed by sulphydric acid; and the filtrate is neutralised with magnesium carbonate, again filtered, and evaporated to the consistence of an extract.

* Zeitschr. f. Chem. [2], vii, 88, from Ann. Ch. Pharm., clvi, 190.

† Zeitschr, f. Chem. [2], vii, 86, from Ann. Ch. Pharm., clvi, 181.

The residue is repeatedly extracted with alcohol so long as the solution possesses rotatory power: the solution is evaporated, the residue is extracted with small quantities of alcohol (not absolute); the solution is treated with animal charcoal and poured in a thin stream into a mixture of absolute alcohol and ether. The bulky, white, amorphous precipitate is quickly filtered off, washed with a mixture of alcohol and ether, and dried in a vacuum.

Synanthrose, $C_{12}H_{22}O_{11}$, is isomeric with cane-sugar, deliquescent; easily soluble in water and dilute alcohol; difficultly soluble in absolute alcohol; insoluble in ether; optically in active; does not reduce the solution of copper or does so only after it has become altered by boiling. Dilute acids convert it into dextrose and lævulose: the rotatory power of inverted synanthrose is $\alpha = -54{\cdot}09°$, and is not influenced by temperature: the flavour of synanthrose is faint but not sweet, that of the inverted sugar being sweet. It is not directly fermentable; yeast acts upon it indeed, but only after splitting it into dextrose and lævulose. At 140°—145° it turns brown, evolves gas, and passes into caramel, glucose and lævulosan, the latter apparently optically inactive. Cold caustic alkalies do not turn it brown. Cold concentrated sulphuric acid produces less colour with it than with cane-sugar. Silver nitrate in the cold gives a white precipitate, which is reduced on heating, and partially on drying. Copper salts and mercuric chloride give no precipitate, mercuric nitrate gives a bulky white precipitate without reduction. Mercurous nitrate and Millon's solution are at once reduced in the cold. Neutral and basic lead acetate give no precipitate; lime and baryta water give precipitates only on addition of alcohol. Synanthrose does not combine with sodium chloride or other neutral salts; is decomposed by chlorine and hypochlorites; and gives by dry distillation, carbon oxide and dioxide, marsh gas, acetic acid, and acetone. It forms a hydrate, $C_{12}H_{22}O_{11} + H_2O$, the water in which cannot be driven off in the air-bath without decomposition of the synanthrose; it appears to form a similar compound with alcohol. The barium compound, $C_{12}H_{19}O_{11}Ba$, easily decomposed by carbon dioxide, is difficultly soluble in water, insoluble in alcohol, and easily soluble in dilute acids. The lead compound, $C_{12}H_{18}O_{11}Pb$, is more stable than the barium compound, and dissolves easily in acetic acid or leadacetate.

Synanthrose interferes with the precipitation of copper, iron, and chromium oxides. Ferric oxide freshly precipitated in the cold dissolves in solution of synanthrose, and by evaporation is reduced to magnetic oxide, glucose being also formed. By treatment with chromic acid or lead dioxide, it yields formic acid. With hot dilute nitric acid, it gives saccharic and oxalic acids.

On treatment with a cold mixture of 1 p. concentrated nitric acid and 2—2½ p. sulphuric acid, an explosive nitro-compound, soluble in

alcohol, less soluble than pure synanthrose in water, is formed. Acetic, butyric, and tartaric acids at 100° produce glucose-compounds. The prolonged action of sulphuric and hydrochloric acids produces glucic acid, and, finally, humus-compounds.

F. H. H.

On some derivatives of Thymol. By E. CARSTANJEN.*

THE author, having observed that diamidothymol, $C_{10}H_{11}(HO)(NH_2)_2$, is readily converted by the action of oxidising agents into a non-nitrogenous body having the empirical formula $C_{10}H_{12}O_3$, and possessing the characters of an oxyquinone derived from the hydrocarbon $C_{10}H_{14}$, was led to an experimental revision of the scanty observations which have as yet been published on the quinone and other allied bodies of the thymol or thymo-cymolic series.

Lallemand† obtained, by the direct oxidation of thymol with manganese dioxide and sulphuric acid, well-characterised compounds similar in properties to quinone and hydroquinone from quinic acid, but having formulæ which did not stand in any simple relation to that of thymol. To these bodies, called by him thymoïl and thymoïlol, Lallemand assigned the formulæ $C_{12}H_{16}O_2$ and $C_{12}H_{18}O_2$. He described also an intermediate product to which he gave the name thymeïd and the formula $C_{24}H_{34}O_4$, and a body, oxythymoïl, $C_{12}H_{16}O_3$, obtained from thymoïl by the action of direct sun-light.

To prepare the so-called thymoïl, the author exposes a mixture of 60 grms. of pure thymol and 40 grms. of strong sulphuric acid to the temperature of 50°—60°, constantly stirring. The thymol first melts and turns slightly brown, and after a short time the mixture solidifies to a mass of reddish-white hard crystals of thymolsulphuric acid. This is dissolved in 6 or 8 times its weight of boiling water; the solution is filtered through a moistened filter to remove traces of unaltered thymol, and the clear liquid is mixed with 40 grms. more of strong sulphuric acid and then distilled with excess of manganese dioxide. Pale-yellow oily drops pass over with the aqueous vapour and solidify in the condenser to a crystalline mass, which may be purified by crystallisation from alcohol or ether-alcohol, or better by distillation *per se*, the first portions then passing over without decomposition. The yield does not exceed 35 p. c.

The body thus obtained crystallises in fine yellow prismatic tables, having a marked vitreous lustre. It has a penetrating and quite peculiar aromatic odour. It melts at 45·5° (48° Lallemand), evolves yellow vapours when further heated, and ultimately boils at about 200°, without decomposition. It is soluble with great difficulty in water,

* J. pr. Chem. [2], iii, 50—68.

† Ann. Chem. Pharm., ci, 119; cii, 119.

but easily in alcohol and ether, even in the cold. It dissolves in strong sulphuric acid and in fuming nitric acid, without alteration in the cold, and is thrown down from the solutions by water. The author's observations fully confirm Lallemand's statements as to its behaviour with caustic alkalies and ammonia.

Analyses of the pure and dry substance gave 72·5 to 73·2 p. c. C., and 7·5 to 7·7 H. The formula $C_{10}H_{12}O_2$ requires 73·2 p. c. C. and 7·3 H. The compound is, therefore, evidently the quinone derived from the hydrocarbon $C_{10}H_{14}$, and is named by the author *thymoquinone.* Lallemand's formula, $C_{12}H_{16}O_2$, requires 75·0 p. c. C.

When thymoquinone, suspended in water, is treated with a current of sulphur dioxide, till completely saturated, the yellow compound assumes a shining black appearance, and after standing for 3 or 4 days becomes converted into a dirty-white crystalline powder, which dissolves easily in alcohol and ether. The new compound dissolves with great difficulty in cold water, but with moderate facility in boiling water, from which it crystallises perfectly pure. From water containing a little sulphurous acid it crystallises in transparent, beautiful, glassy, heavy crystals, a combination of the four-sided prism with two pyramids. This body is *hydrothymoquinone* (Lallemand's thymoïlol). It melts at 139·5° (145° Lallemand) and sublimes undecomposed at higher temperatures. It gave on analysis, 71·8 to 72·2 p. c. C., and 8·5 to 8·7 H., the formula $C_{10}H_{14}O_2$ requiring 72·3 p. c. C. and 8·4 H. Lallemand's formula, $C_{12}H_{18}O_2$, requires 74·2 p. c. C. and 9·3 H.

Hydrothymoquinone is easily converted into thymoquinone by ferric chloride, nitric acid, &c. As is mentioned above the first action of sulphurous acid on thymoquinone is to form a black shining body which corresponds to the quinhydrone of the benzene series (Lallemand's thymeïd). This body, named by the author *thymoquinhydrone*, is best obtained by mixing alcoholic solutions of thymoquinone and hydrothymoquinone: on spontaneous evaporation of the liquid it is deposited in perfectly black, beautiful, shining needles.

Action of Bromine on Thymoquinone.—When thymoquinone is heated with two molecules of bromine under water till the smell of bromine is no longer perceptible, a clear dark-red oil is formed, which, after repeated washing with cold water, speedily solidifies to a hard yellowish-red crystalline mass, consisting of a mixture of mono- and di-brominated thymochinone.

Dibromothymoquinone, $C_{10}H_{10}Br_2(O_2)''$.—The crystalline mass dissolves with tolerable facility in boiling alcohol, the solution depositing, as it cools, an abundance of fine lustrous pale-yellow laminæ, which are obtained perfectly pure by washing with cold alcohol. In the dry state the substance forms extremely light shining pale-yellow laminæ, resembling chloranil. It melts to a pale-yellow liquid at 73·5°. On

exposure to light it gradually assumes a reddish colour. It gave on analysis 36·8 p. c. C., 3·6 H., and 49·4 to 50·0 Br.; the above formula requiring 37·3 p. c. C., 3·1 H., and 49·7 Br. When treated with tin and hydrochloric acid, the group $(O_2)''$ is converted into $(OH)_2$, the bromine being at the same time displaced by hydrogen, so that normal hydrothymoquinone is produced.

Monobromothymoquinone, $C_{10}H_{11}Br(O_2)''$.—The mother-liquor of dibromothymoquinone contains a much more soluble substitution-product, which crystallises in long yellow needles on spontaneous evaporation of the solution. The author was unable to obtain this body quite free from the foregoing, determinations of the bromine giving 35·3 to 36·1 p. c., instead of 32·9 p. c., as required by the above formula. The impure compound dissolves with brownish-red colour in warm aqueous potash-ley: dilute acids throw down from the solution a yellow flocculent powder, which, after drying, sublimes in splendid scarlet crystals. This body is oxythymoquinone, $C_{10}H_{11}(HO)(O_2)''$, the formation of which confirms the existence of monobromothymoquinone.

Oxythymoquinone, $C_{10}H_{11}(HO)(O_2)''$.—The author has also obtained this body by a process totally different from that just described, namely, by distilling diamidothymolhydrochloride, $C_{10}H_{11}(HO)(NH_2)_2.(HCl)_2$, with ferric chloride in a current of steam. The reaction in this case evidently resembles that observed by Gräbe and Ludwig* in the case of diamidonaphthol.

Oxythymoquinone crystallises from hot alcohol, in which it is easily soluble, in perfectly regular rhombic tables, the angles of which approximate to those of the cube, and from ether in irregular crystals, having curved faces. It melts at 187° (uncorr.) in a capillary tube, and sublimes without decomposition in splendid glittering scarlet crystals.

As might be expected from the accumulation of electronegative groups, the hydrogen of the hydroxyl is not displaceable by acetyl, the substance being unacted upon by acetyl chloride. On the other hand this hydrogen is readily displaced by basic radicals. Oxythymoquinone is converted by ethyl iodide at 100° into *ethoxythymoquinone*, $C_{10}H_{11}(C_2H_5.O)(O_2)''$, a well-characterised substance subliming completely in golden-yellow laminæ. Aniline in alcoholic solution also acts immediately upon a solution of oxythymoquinone; the liquid assumes a dark purplish-brown colour, and after evaporation the residue yields by sublimation beautiful violet needles having a brilliant metallic lustre, melting to a purple liquid above 200°, and dissolving very freely in alcohol. Analyses of oxythymoquinone gave 66·1 to 66·7 p. c. C., and 6·7 to 7·4 H., the formula requiring 66·6 p. c. C., and 6·7 H. The substance is acted upon with difficulty by reducing agents. On warming it with tin and hydrochloric acid, the group $(O_2)''$

* Ann. Ch. Pharm., cliv, 303.

appears to be reduced to $(HO)_2$, *oxythymohydroquinone*, $C_{10}H_{11}(HO)_3$, being thus formed. This body forms a white crystalline mass, easily soluble in water, forming a solution which instantly turns yellow and deposits oxythymoquinone on exposure to air.

Dioxythymoquinone, $C_{10}H_{11}(HO)_2(O_2)''$.—This substance is formed when dibromothymoquinone, moistened with alcohol, is dissolved in warm potash-ley, and the dark-brown solution is decomposed by dilute acids. The brownish-yellow flocks thereby thrown down, after being washed with hot water, dissolve in warm alcohol, which deposits crystals on evaporation, always contaminated, however, with a brown resinous substance, difficult to separate. The pure substance has not yet been analysed.

Constitution of Thymol and its derivatives.—The question as to the constitution of thymol has recently assumed a perfectly definite form. The researches of Engelhardt and Latschinoff (who observed that thymol is resolved by phosphorus pentoxide into γ-cresol and propylene) showed that it may certainly be regarded as a methyl-propyl-phenol. But on the other hand neither Pott* nor Müller† succeeded in obtaining thymol from the known methyl-propyl-benzenes, and the question as to the relative positions of the alcohol-radicals (lateral chains) so easily answered in the case of the isomeric cymenes, remained undecided. The facility with which the position of the alcohol-radicals in non-oxygenated derivatives of benzene is determined, induced the author to attempt to obtain the hydrocarbon of which thymol is the hydroxyl-derivative. With this object thymol was warmed with a mixture of phosphorus oxychloride and pentachloride. The yellow oily body thus obtained, when treated in slightly acid solution with sodium-amalgam, yielded with difficulty a small quantity of a limpid hydrocarbon, which was ultimately purified by rectification off sodium.

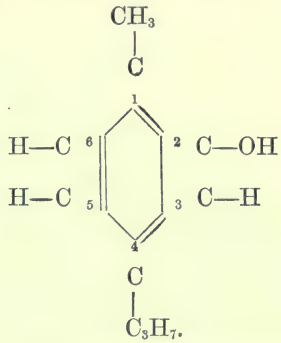
The hydrocarbon (*thymo-cymene*) possesses an agreeable odour of thyme. It does not solidify in a freezing-mixture, and boils, apparently, at 173°. Analysis gave 89·1 p. c. C. and 10·6 H., the formula $C_{10}H_{14}$ requiring 89·5 p. c. C. and 10·5 H. When boiled with potassium dichromate and sulphuric acid, it was gradually oxidised to a white pulverulent, apparently amorphous acid, which, after being dissolved in ammonia and re-precipitated by hydrochloric acid, was perfectly white, insoluble in water, alcohol, and ether, and non-fusible. This body gave on analysis the numbers of benzene-dicarbonic acid, $C_6H_4.(CO_2H)_2$ (57·4 p. c. C., 3·8 H., theory requiring 57·8 p. c. C., 3·8 H.,), and is characterised by its properties as terephthalic acid.

The position of the radicals (lateral chains) in the benzene-dicarbonic acids being, in phthalic acid 1 : 2 (ortho), in isophthalic acid 1 : 3

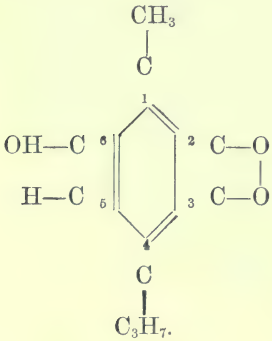
* Zeitschrift für Chemie [2], v, 200.

† Deut. Chem. Ges. Ber., 1869, 130.

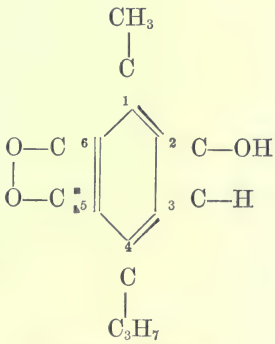
(meta), in terephthalic acid 1 : 4 (para), it follows that the position of the alcohol-radicals methyl and propyl (or iso-propyl) in thymol must be 1 : 4. On Kekulé's hypothesis the body may, consequently, be represented by this formula:—



In thymoquinone, the two quinone oxygen-atoms doubtless occupy the positions 2 and 3, the oxygen of the hydroxyl already present having taken part in the formation of quinone. In monobromothymoquinone the bromine displaces the hydrogen-atom occupying the position 6, that is, the atom opposite to the original hydroxyl-group in thymol. In diamidothymol, as in the dinitrothymol from which it is derived, the nitrogenous radicals occupy the positions 5 and 6, the behaviour of the substance showing that they are in direct combination with contiguous carbon-atoms. The oxythymoquinone obtained from this compound is, as experience has shown, perfectly identical with that obtained from monobromothymoquinone, an identity which is well expressed in the following formulæ:—



Oxythymoquinone, from Monobromothymoquinone.



Oxythymoquinone, from Diamidothymol.

J. R.

The Nitration of β-Naphthol. By O. WALLACH and H. WICHELHAUS.*

WHEN β-naphthol† is dissolved in a considerable quantity of alcohol, and heated to 100° C. with excess of dilute nitric acid, the solution acquires a dark-red colour and deposits a small quantity of resinous matter. After the greater portion of the alcohol has been removed by distillation, the addition of water causes an abundant flocculent precipitate. This deep-red precipitate is now treated with soda-solution, which leaves undissolved the resinous portion, and the clear liquid is precipitated by hydrochloric acid, the precipitate dissolved in alcohol with addition of animal charcoal, again separated by dilution with water, and, after further treatment with animal charcoal, repeatedly crystallised from chloroform until it forms distinct needles of a bright-yellow colour. This substance, *dinitro-β-naphthol*, $C_{10}H_5(NO_2)_2OH(\beta)$, crystallises in tufts of glistening needles, appearing under the microscope as truncated prisms, which turn brown, and melt at 195° (dinitro-α naphthol melts at 138°). It is but slightly soluble in water, even when boiling, more so in alcohol, and very easily in ether and chloroform. Its solutions, and those of its salts dye yellow. Its salts are more difficult to obtain than those of the α compound. The addition of ammonia colours the crystals bright red, and the boiling solution deposits the ammonium salt in red needles, which partly decompose on exposure to the air. The addition of silver-salts to this solution produces a scarlet, flocculent precipitate, and barium salts a bright yellow one; the latter when crystallised from boiling water, forms thin, flexible, lustrous needles, which become red at 100°. All the salts are soluble with difficulty. Like its isomerite from α-naphthol, it does not appear to form compounds with hydrocarbons.

C. E. G.

Naphthazarin. By C. LIEBERMAN.‡

Naphthazarin, $C_{10}H_6O_4 = C_{10}H_4O_2(OH)_2$, prepared by Roussin's method gives with baryta- and lime-water fine violet-blue precipitates; with magnesia, a crimson; with basic acetate, a blue; and with ferric salts a black precipitate. Ammonia dissolves naphthazarin with a sky-blue colour, which by long standing changes to a reddish-violet; concentrated sulphuric acid gives in the cold, a beautiful magenta-coloured solution from which water precipitates red flocks. It is soluble with

* Zeitschr. f. Chem. [2], vii, 48, from Deut. Chem. Ges. Ber., iii, 816.

† β-naphthol, free from α-naphthol may be obtained by heating 200 grms. naphthaline and 180 sulphuric to 160° C. for seven hours, neutralising with soda, and fusing the product.

‡ Zeitschr. f. Chem. [2], vii, 56, from Deut. Chem. Ges. Ber., iii, 905.

difficulty in boiling water, but more easily in alcohol, from which it crystallises. By heating it with zinc dust the author obtained naphthalene. Roussin's dye is therefore *dioxynaphtho-quinone.*

C. E. G.

On the Same. By A. A. de Aguiar and Al. G. Bayer.*

The object of the authors was to determine from which modification of dinitronapthalene this body is derived. Both modifications α and β were used in the state of the utmost purity.

Their first experiments were made on the modification α (crystallising in six-sided needles and melting at 214° C.); from this substance was prepared naphthazarin according to the directions of Roussin as given by Liebermann; but somewhat less zinc was employed, as the reaction appeared to the authors generally to go too far. The dinitronaphthalene was added to sulphuric acid heated to 200°, and then the zinc in small portions; the temperature was retained constant for about twenty minutes, and then the mixture allowed to cool; when cold it was treated with boiling water and allowed to stand for 48 hours. The precipitate was then filtered off, slightly washed with cold water, and treated with strong aqueous potash; any traces of unaltered dinitronaphthalene could now be removed by filtration. The beautifully coloured blue liquid was now supersaturated with dilute sulphuric acid, whereby the crude naphthazarin was slowly precipitated; it was then filtered off and dried at 100°. Great difficulty was experienced in separating the naphthazarin from a black secondary product of the reaction; a process of sublimation was attempted, but 6 grms. of crude naphthazarin yielded only 0·35 grm. of sublimate. The body may, however, be obtained very nearly pure by solution in glacial acetic acid, the black body remaining undissolved. The acetic acid is to be distilled off from a sand-bath at a temperature slightly exceeding 100° C.

Thus prepared, naphthazarin is a crystalline mass having a green metallic lustre, and exhibiting the already known colour reactions, giving a blue colour with ammonia and a beautiful red with sulphuric acid, &c.

The authors endeavoured to examine the above-mentioned black body, but found great difficulty in doing so, because it is unattacked by almost all solvents; they therefore endeavoured to extract all the naphthazarin from it by boiling with glacial acetic acid. If this operation was carried on in open vessels, the acid was coloured red with a tinge of violet; this colouring was not due to naphthazarin, because no blue colour was produced on addition of ammonia.

* Deut. Chem. Ges. Ber., iv, 251—253.

The black body appeared to be a nitrogen-compound, intermediate in composition between dinitronaphthalene and naphthazarin: it contained about 6 per cent. of nitrogen.

If in the preparation of naphthazarin, the zinc was omitted, the same result was obtained, but a longer time was required. Persoz's statement that a higher temperature is required when the zinc is omitted, was not confirmed by the authors. They found that no sulphurous acid was liberated when zinc was not employed, but that it was liberated on the use of zinc. They state that a product more free from the black body was obtained without the zinc.

Bubbles of gas escaped during the whole operation, but neither nitrous acid nor nitrous oxide could be detected. The authors point out that dinitronaphthalene minus nitrogen equals naphthazarin—

$$C_{10}H_6(NO_2)_2 = C_{10}H_4(HO)_2O_2 + N_2.$$

They suggest, therefore, that the escaping gas was nitrogen, and hope to determine it quantitatively in a future paper, when they will make a communication on the colouring matter which they have obtained from β-dinitronaphthalene.

E. T. C.

Nitro-substitution Compounds of the Orcins. By JOHN STENHOUSE.*

THE author first notices the comparatively negative results, which have hitherto been obtained by the action of nitric acid on orcin, yielding, as they do, resinous uncrystallisable substances, and ultimately oxalic acid. He then proceeds to describe the method by which he succeeded in obtaining a crystalline nitro-compound.

Colourless orcin, prepared from ordinary orcin by distillation *in vacuo*, was dissolved in a small quantity of water, and this solution gradually added to strong nitric acid, which had been cooled to a temperature of $-10°$ C. The pale brown solution thus obtained was now added, with constant stirring, to concentrated sulphuric acid, also maintained at a temperature of $-10°$ C., and the resulting pasty mass, after remaining in the freezing mixture for fifteen or twenty minutes, was poured into a mixture of water and crushed ice; the crude nitro-orcin was thus precipitated as an orange-coloured granular powder. The amount obtained was 150 per cent. of the weight of the orcin.

One or two recrystallisations from boiling water rendered the nitro-orcin pure. It then forms large yellow needles, which are readily soluble in hot water, but slightly in cold, and still less so in dilute acids. It is soluble in alcohol, very soluble in hot benzol, and crys-

* Proc. Roy. Soc., xix, 410—418.

tallises out in great part on cooling; less soluble in ether, and but moderately so in carbon bisulphide. It dyes the skin yellow like picric acid, but is tasteless. It volatilises slightly at 100°, melts at 162°, and decomposes with slight explosion immediately afterwards. When heated with concentrated sulphuric acid, it dissolves, forming a deep yellow solution, which deposits crystals on cooling, and is immediately precipitated by water. It dissolves in hot, strong nitric acid, with evolution of nitrous fumes and formation of oxalic acid. It yields chloropicrin, when treated with calcium hypochlorite, at the ordinary temperature. Its aqueous solutions are coloured dark brown by ferric chloride, and completely precipitated by lead subacetate. The results of the analysis correspond with the formula $C_7H_5(NO_2)_3O_2$. This *trinitro-orcinic acid* is a powerful acid much resembling picric acid.

The *potassium salt*, $\left.\begin{matrix}C_7H_3(NO_2)_3\\K_2\end{matrix}\right\}O_3$, was prepared from potassium carbonate and trinitro-orcinic acid. It is very soluble in hot water, and crystallises in needles of a deep orange colour. The *sodium salt*, like the potassium salt, forms orange-coloured needles; the *ammonium salt* forms deep yellow silky needles, which are very soluble in water, but much less so in alcohol. The *barium salt*, $\left.\begin{matrix}C_7H_3(NO_2)_3\\Ba\end{matrix}\right\}O_2 + 3H_2O$, was prepared by neutralising a boiling solution of 1 part of nitro-orcin in 500 of water, with barium carbonate: it forms bright yellow needles, which lose their water of crystallisation at 100°, and become orange-red. The *calcium salt* forms yellow needles which are very soluble in hot water. The *magnesium salt* is very soluble in cold water, and crystallises in minute orange needles. The *lead salt*, $\left.\begin{matrix}C_7H_3(NO_2)_3\\Pb\end{matrix}\right\}O_2$, prepared by precipitating a very dilute aqueous solution of nitro-orcinic acid with an acidulated solution of lead acetate, forms tufts of microscopic needles, which are almost insoluble in cold water; slightly in hot. It crystallises unaltered from hot acetic acid. The *copper salt* is very soluble in water and alcohol, and crystallises in reddish-brown needles; the *zinc salt* forms tufts of yellow needles, which are likewise very soluble. The *silver salt*, $\left.\begin{matrix}C_7H_3(NO_2)_3\\Ag_2\end{matrix}\right\}O_2$, prepared from the acid and silver oxide, forms an orange-red, gelatinous mass, which exhibits no signs of crystallisation. It is slowly decomposed by long boiling.

Ethyl trinitro-orcinate $\left.\begin{matrix}C_7H_3(NO_2)_3\\(C_2H_5)_2\end{matrix}\right\}O_2$, prepared by boiling the silver salt with excess of ethyl iodide, crystallises from alcohol in bright yellow prismatic needles, which melt at 61°·5. *Methyl trinitro-orcinate* very closely resembles the ethyl compound, but melts at 69°·5.

Trinitro-resorcinic acid, $C_6H_3(NO_2)_3O_2$, was prepared from resorcin

in a manner precisely similar to that previously described for obtaining nitro-orcin. When pure it melts at 175°·5, and is soluble in 156 parts of water at 14°.

The *barium salt*, $\left.\begin{matrix}C_6H(NO_2)_3\\ Ba\end{matrix}\right\}O_2 + 3H_2O$, is much more soluble than the nitro-orcin compound, and was prepared by neutralising a solution of one part of nitroresorcin on 100 of boiling water with barium carbonate. It forms rhomboïdal plates of a pale yellow colour, which do not lose their water of crystallisation at 100°. When heated on platinum-foil it explodes with great violence. Both nitro-orcinic and nitro-resorcinic acids and their salts explode with far greater violence than picric acid and its compounds.

The *lead salt* is obtained, on boiling a very dilute solution of the acid with excess of lead carbonate, in the form of deep yellow needles. It is but slightly soluble in water. Subacetate of lead completely precipitates solutions of trinitro-resorcinic acid.

The silver salt, $\left.\begin{matrix}C_6H(NO_2)_3\\ Ag_2\end{matrix}\right\}O_2$, prepared in a similar manner to the nitro-orcinate, crystallises in slender needles of a yellowish-brown colour.

Trinitro-beta-orcinic acid appears to be produced by treating beta-orcin, $C_8H_{10}O_7$, with nitric and sulphuric acids in the manner previously described, but the author has not yet investigated its properties.

C. E. G.

On Butyric Acid from Different Sources. By C. Grünzweig.*
(Preliminary notice.)

The acid obtained from butter and by oxidation of conine is the normal, that from the carob, *Ceratonia siliqua*, the iso-acid.

The distillate from tamarinds seems to be free from butyric acid.

F. H. H.

On the Fatty Acids contained in Hungarian Wine Fusel-Oil, and on some Derivatives of Capric Acid. By Ferdinand Grimm.†

The crude fusel-oil, which was obtained from Pesth, had a dark hock colour, and a strong, unpleasant, nauseous smell. From 25 lbs. the water, ethyl alcohol, and amyl alcohol were removed by distillation, and the residue (a little more than one-half of the original liquid) was boiled with a strong solution of caustic soda. To the lower layer, which contained the sodium salts of the fatty acids, dilute sulphuric acid was added; a brown oil, having a very unpleasant smell, separated,

* Ann. Ch. Pharm., clviii, 117.

† Ann. Ch. Pharm., clvii, 264—274.

which was dissolved in dilute ammonia. A fatty substance was left behind, which was removed, and the liquid precipitated by barium chloride. The precipitate was collected on a linen cloth and pressed between filter-paper. In order to remove the fatty substance, which still stuck to it, the barium salt was decomposed by hydrochloric acid, and the fatty acids were saponified with a dilute solution of sodium carbonate. After repeating this operation twice, a mixture of fatty acids was obtained, which solidified at + 20°. On distillation, it began to boil at 225°, the temperature rising gradually to 280°, when a thick brown residue was left in the retort.

A small portion of the distillate was precipitated in fractions by a hot concentrated solution of caustic baryta. The analysis of the different fractions showed that the acids consisted chiefly of capric acid with a little caprylic and perhaps a small quantity of œnanthylic acid. The same acids were found by Fischer in crude œnanthic ether, with the only difference that he obtained more caprylic acid.

It is certainly remarkable that no pelargonic acid (standing between caprylic and capric) could be detected. The author thinks it possible that this acid, which is very little known, is perhaps only a mixture or loose combination of caprylic and capric acids, corresponding to butyro-acetic acid.

To obtain pure capric acid, the mixture of acids was subjected to fractional distillations, and the portion boiling above 260° pressed between filter-paper, first at a very low, and afterwards at the common temperature.

Pure capric acid melts at 30° to a clear oil, which begins to solidify again at 29·5°; it boils with partial decomposition at 268°—270°.

The following derivatives were prepared by the author:—

Methyl caprate, $C_{10}H_{19}O.CH_3O$, was obtained by saturating a solution of the acid in methyl alcohol with dry hydrochloric acid gas. It is a colourless liquid, boiling at 222°—225°, and possessing a pleasant fruit-like smell. *Ethyl caprate*, which has been prepared by Fischer and Rowney, boils at 243°.

Amyl caprate, $C_{10}H_{19}O.C_5H_{11}.O$, prepared by acting with hydrochloric acid on a solution of the acid in amyl alcohol, is a light colourless liquid, which has only a faint smell. The small quantity which the author obtained distilled between 275°—290° with partial decomposition. This ether is contained in large quantity in the Hungarian fusel-oil, which contains neither propyl nor butyl alcohol.

Caprone, or Dinonyl-ketone, $CO(C_9H_{19})_2$, is obtained in large quantities by distilling the calcium salt of the acid. It crystallises in white pearly scales, which are insoluble in water, readily soluble in ether and boiling alcohol. It melts at 58°, solidifies again at 56°, and boils above 350°. It is not acted upon by a boiling mixture of 8 parts of

potassium dichromate, 3 parts of sulphuric acid, and 10 parts of water; neither is it changed by dilute nitric acid; when it is heated with concentrated nitric acid a violent action takes place, and, amongst other products, capric acid, and perhaps also caprylic acid, are formed.

Capryl chloride, $C_{10}H_{19}O.Cl$. The preparation of this compound was tried by the three usual methods, viz., by acting with phosphorus tri- and penta-chloride on the acid, and by treating the barium-salt with phosphorus oxychloride. The best results were obtained with the penta-chloride, but the compound could not be obtained in the pure state, as it is decomposed by distillation, and violently acted upon by water. It is a heavy liquid, boiling above 200°; its odour is not pungent, but faintly aromatic.

Besides this compound a white crystalline body was formed by the reaction; the quantity was too small to study it properly; as it is not acted upon by boiling water, nor a solution of potash, it could not be the anhydride of the acid.

C. S.

Further Observations on the Constitution of Diglycollic, Diglycollamic, and Triglycollamic Acids. By W. HEINTZ. (*J. pr. Chem.* [2], iii,120). On the same Subject. By A. CLAUS. (*Ibid.*, 123).

On the Purification of Ethylenelactic Acid by means of a double Zinc-calcium Salt. By W. HEINTZ.*

HEINTZ, by mixing a concentrated solution of calcium ethylenelactate with a solution of the zinc salt, has obtained a double compound, which gave, on analysis, numbers agreeing with the empirical formula $C_{12}H_{20}CaZnO_{12}$. The comparative insolubility of this body seemed to fit it for the purification of the acid. This can be carried out as follows:—

The impure free acid is divided into two parts, one of which is saturated with lime, the other with zinc oxide, and the solutions are mixed together. With sufficiently concentrated solutions, some of the double salt is precipitated at once; the remainder can be obtained by evaporating the mother-liquor. The salt is well washed, and crystallised. The zinc is removed by passing hydrogen sulphide through its solution; and after that, the lime is precipitated by an equivalent quantity of oxalic acid. By this method pure ethylenelactic acid was obtained in considerable quantity, when crystallisation of the impure calcium salt had failed.

The calcium-zinc compound can be obtained in small crystals, by allowing its solution in a small quantity of hot water to evaporate

* Ann. Ch. Pharm., clvii, 291—295.

over sulphuric acid. The crystals require 11·5 pts. of water at 15° to dissolve them: they are not much more soluble in boiling water. They are quite insoluble in boiling ether or alcohol.

W. H. D.

On the Nature of the Lactic Acid obtained from Flesh. By W. HEINTZ.*

THE observation of Wislicenus, that ethylene-lactate and ethylidene-lactate can be obtained by treating zinc sarcolactate with alcohol, coupled with the ready formation of a double salt of calcium acrylate with calcium ethylene-lactate, led Heintz to consider that the sarcolactates might prove to be double salts of ethylene- and ethylidene-lactic acids.

By mixing solutions of zinc ethylene-lactate and zinc ethylidene-lactate in equivalent proportion, a small quantity of a salt was obtained, which lost at 105°, 12·81 per cent. water, equal to two molecules. At 14°, one part of the salt required 6·2 pts. water to dissolve it, a number closely approaching that obtained for the sarcolactate. The salt was not a simple mixture of ordinary crystallised ethylene- and ethylidene-lactates, as the former contains 4 molecules water, the latter 3 molecules water.

Notwithstanding this agreement, however, the body in question is only a double salt, not the sarcolactate. The salts of sarcolactic acid have, as was shown by Wislicenus, the power of turning the plane of polarisation to the left; this power was entirely wanting in the double salt. Moreover the crystals deposited from an aqueous solution of the double salt, show an increase in the percentage of water, more approaching that of zinc ethylidene-lactate as the crystallisation is more frequently repeated. This is not the case with the sarcolactate.

The author thinks it possible that ethylene-lactic acid and ethylidene-lactic acid may be connected in zinc sarcolactate, somewhat in the same way as dextro- and lævo-tartaric acids in racemic acid.

W. H. D.

On the Products of Decomposition obtained by boiling Chlorethylidene-propionic Acid and Iodethylenepropionic Acid with Milk of Lime. By W. HEINTZ.†

THE author desired to discover whether, by the above treatment, a dilactic acid would be produced, as well as a lactic acid.

By boiling chlorethylidenepropionic acid with an excess of milk of lime, calcium ethylidenel-actate (containing 5 molecules of water of crystallisation) was obtained, but no dilactate was produced.

* Ann. Ch. Pharm., 314—323.

† Ann. Ch. Pharm., clvii, 295—314.

Iodethylene-propionic acid was boiled for between one and two hours, with rather more milk of lime than was necessary for its conversion into calcium lactate and iodide. The decomposition was complete in this time; the whole amount of iodine could be precipitated by silver nitrate. From this liquid a crystalline substance was obtained, which showed a percentage composition corresponding to $C_6H_8CaO_5 + H_2O$, the water of crystallisation being given off at 110°. This body, although it has the composition of a dilactate, was shown by numerous experiments not to be so, but a double compound of calcium acrylate and calcium ethylene-lactate. Oxalic acid liberates the two acids from its solution; silver nitrate added to the solution of the double salt throws down silver acrylate. That the acrylic and lactic acids are not produced by the breaking up of an acid, is shown by the formation of the double calcium salt, similar in all its properties to the original body, by neutralising with lime a mixture of acrylic and ethylene-lactic acids, in equivalent proportions.

In addition, an extremely small quantity of a body only slightly soluble in water, was obtained by the action of lime on iodethylene-propionic acid. From 200 grms. iodopropionic acid employed, only a few decigrams of this body were obtained. It crystallised in small, microscopic needles; melted between 50° and 60°, and had an acid reaction. The analytical results indicated $C_{18}H_{26}O_{13}$ as the formula of this substance. A further examination of it could not be made, from lack of material. It may have been produced by the fixation of one molecule of water by six molecules of acrylic acid: $6C_3H_4O_2 + H_2O = C_{18}H_{26}O_{13}$.

Heintz concludes from these experiments, that by boiling iodethylene-propionic acid with milk of lime, there are formed: a small quantity of a difficultly soluble acid, no diethylene-lactic acid, but ethylene-lactic and acrylic acids.

W. H. D.

On the Isomerism of Aromatic Acids. By H. Huebner.*

The following researches, which the author carried out in conjunction with his pupils, are a continuation of former experiments:—

1. *On Mono- and Dibromo-benzoic Acid*, by Ed. Angerstein. By acting with bromine upon benzoic acid, Peligot obtained a bromobenzoic acid, melting at 100°; this might be the still missing metabromobenzoic acid (bromsalylic acid), as the ortho-acid melts at 153°, and the para-acid at 251°. The author repeated Peligot's experiments, and found that when silver benzoate is acted upon by bromine vapour in sunlight, only orthobromobenzoic acid is formed, which is gener-

* Ann. Ch. Pharm., clviii, 1—36.

ally mixed with benzoic acid, as the silver salt is apt to retain moisture. Peligot obtained such a mixture, which melts at a lower temperature than either benzoic acid or orthobromobenzoic acid (see next paper). The reaction by which this acid is formed is the following—

$$C_6H_5CO_2Ag + Br_2 = C_6H_4BrCO_2Ag + HBr = AgBr + C_6H_4BrCO_2H.$$

The identity of the acid thus formed with that obtained by the action of bromine on benzoic acid, was proved by determining the melting point (152°—153°) and by comparing the barium salts of the two acids; both form small, smooth needles, containing 4 molecules of water. The nitro-acids are likewise identical: the sodium salt exhibited all the characteristic properties of sodium β-bromnitrobenzoate; it crystallised from a concentrated solution in long needles, forming an almost solid magma, which on stirring, changed into small plates: on touching a concentrated solution of the latter with a crystal, long, flat plates at once crystallised out. On boiling the nitro-acid with tin and hydrochloric acid, only metamidobenzoic acid was formed.

The best method of preparing dibromobenzoic acid is to enclose 5 grms. of benzoic acid and 13·1 grms. of bromine in tubes, half filled with water and to heat them to 200°—230°, until the colour has nearly disappeared. The mixture of mono- di- and tri-brombenzoic acid is boiled with water and barium carbonate, and the solution concentrated. Tribromobenzoate then crystallises out first, and afterwards impure dibromobenzoate; whilst the salt of the mono-bromobenzoic acid remains in the mother-liquor. The complete separation of the three acids is very difficult, and can only be effected by employing large quantities of material.

Barium Dibromobenzoate, $(C_6H_3Br_2CO_2)_2Ba + 2H_2O$ crystallises in fine, short, transparent needles. The *calcium salt* forms shining plates; the *sodium salt* is very soluble, and does not crystallise well, the *silver salt* forms a white, and the *copper salt* a light green precipitate. Pure dibrombenzoic acid is sparingly soluble in water, readily in ether and alcohol, and crystallises in fine, fascicular needles, melting at 223°—227°, and subliming without decomposition.

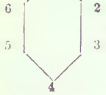
By acting with bromine on silver monobrombenzoate, no dibromobenzoic acid was formed; the product consisted of silver bromide, monobromobenzoic acid, and a few drops of a volatile oil, which attacked the eyes powerfully.

Dibromonitro-benzoic acid, $C_6H_2Br_2.NO_2.COOH$. To prepare the compound, impure dibromobenzoic acid is dissolved in hot concentrated nitric acid. The solution is evaporated on the water-bath, and the residue dissolved in sodium carbonate. As the sodium salt of the

acid crystallises exceedingly well, it is easily obtained by recrystallising the mixture of the sodium salts and rejecting the first crystals and the last mother-liquors. The middle portion yields on further crystallisation the pure salt $C_6H_2Br_2.NO_2.CO_2Na + 3H_2O$, which separates from a hot concentrated solution in large shining leaflets, and from a diluted solution in long fine needles. On heating, it deflagrates, leaving a bulky, carbonaceous mass behind.

Barium Dibromo-nitro-benzoate, $(C_6H_2Br_2.NO_2.COO)_2Ba + 2H_2O$, forms fine silky needles. The *strontium* salt crystallises in very long and fine silky needles. The *lead* and *silver salts* are white precipitates, and the *copper salt* forms a light green precipitate. The *acid* crystallises from water in white needles, which melt at 162°, and deflagrate on further heating.

Dibromamido-benzoic acid, $C_6H_2Br_2.NH_2.COOH$, is obtained by boiling dibrom-nitro-benzoic acid for a short time with tin and strong hydrochloric acid. On adding water to the cold solution the amido acid, which does not combine with hydrochloric acid, is precipitated; it crystallises from boiling water in microscopic needles, and from dilute alcohol in distinct needles: it melts at 196°, and decomposes on stronger heating. The mother-liquor from the preparation of this compound contains *metamido-benzoic acid*.

The author thinks that the results of his investigation agree with the present views on the constitution of benzene and its derivatives; if we represent benzene by a hexagon, each corner of which marks the position of a carbon atom, thus—  and assume that the carboxyl is combined with carbon No. 1, then the radicals in the substituted benzoic acids have the following positions:—

Bromobenzoic acid.	*a*-Bromonitrobenzoic acid.		*β*-Bromonitrobenzoic acid.	
Br	Br	NO_2	Br	NO_2
3	3	2	3	6

Dibromobenzoic acid.	Dibromonitrobenzoic acid.	
Br	Br	NO_2
3 and 5	3 and 5	2

2. *On the Conditions under which Orthobromobenzoic Acid is Formed.* By L. H. Friedburg.*—Huebner and Petermann found that by the action of bromine upon benzoic acid, only orthobromobenzoic acid

* See also Zeitschr. f. Chem. [2], vii, 65.

is formed, whilst V. von Richter obtained, besides this acid, also metabromobenzoic acid, melting at 90°. On repeating these experiments, the author obtained the same result as Huebner and Petermann; the product consisted of orthobromobenzoic acid mixed with unaltered benzoic acid; such a mixture melts often at a lower temperature than either of its constituents. Thus a mixture of two parts of benzoic acid and one part of bromobenzoic acid, has a mean melting-point of 96°, and one consisting of one of benzoic and five of bromobenzoic acid, melts at about 115°.

When pure bromobenzoic acid is fused with caustic potash, a small quantity of an acid having the properties of para-oxybenzoic acid is formed, besides salicylic acid; but this does not prove that the brominated acid is a mixture, as by the action of potash, some phenol may have been formed, and Barth has shown that on fusing phenol with caustic potash, both salicylic and para-oxybenzoic acids are formed.*

The author further confirms the results of Huebner, Ohly, and Philipp, that by treating pure ortho-bromobenzoic acid with strong nitric acid, two isomeric bromonitrobenzoic acids are formed, *α-bromonitrobenzoic acid*, which melts at 250°, and the β-acid melting at 140°.

Orthobromobenzoic acid is also obtained by heating bromine and benzamide† with water in sealed glass-tubes.

As this acid is formed by the action of bromine on benzoic acid, on silver benzoate, and on benzamide, it appears that the three groups COOH, COOAg, $CONH_2$, have the same influence on the position which the bromine atom occupies, and the author thought that perhaps the presence of the group CN might cause the formation of metabromobenzoic acid. On heating benzonitrile, C_6H_5CN, with bromine in closed tubes, a reddish-brown thick liquid was obtained, which was dissolved in alcohol, and the solution diluted with water; microscopic crystals gradually separated out, which were scarcely attacked by caustic potash solution at 120°. From the alkaline liquid a small quantity of an acid was obtained, melting at 230°—235°, which was probably para-bromobenzoic acid. Other attempts to prepare the missing or metabromobenzoic acid, likewise gave only negative results. As Henry has shown, this acid is not formed, as chlorosalylic acid (metachlorobenzoic acid) is, by treating salicylic acid with phosphoric pentabromide, and decomposing the product with water. The author found, like Henry, that only bromosalicylic acid is formed. He tried further to prepare diazometamidobenzoic acid, in order to convert it by the action of hydrobromic acid into metabromobenzoic acid, but did

* Journ. Chem. Soc. [2], ix, 122.

† The author found that pure benzamide melts at 125°, and not at 115°, as stated by Liebig and Woehler.

not succeed in obtaining the diazo-compound, which appears to be a most unstable body. On mixing a solution of the sulphate of metamidobenzoic acid (anthranilic acid) with potassium nitrate in the cold, and adding hydrobromic acid, nitrogen is evolved, but no metabrombenzoic acid is formed; the solution containing only salicylic and nitro-salicylic acids, which shows that the diazo-compound is decomposed by the water before the hydrobromic acid can act upon it.

C. S.

On the Transformation of Bromobenzoic Acid into Isophthalic Acid. By E. Ador and V. Meyer.*

This paper is a continuation of the researches on the synthesis of aromatic acids by Meyer, who had found that on fusing a mixture of potassium sulphobenzoate and sodium formate, *isophthalic acid* is formed. The authors find now that the same acid is obtained by using bromobenzoic instead of sulphobenzoic acid, the reaction taking place according to the equation:—

$$C_6H_4\left\{\begin{matrix}Br\\CO_2H\end{matrix}\right. + HCO_2H = HBr + C_6H_4\left\{\begin{matrix}CO_2H\\CO_2H\end{matrix}\right..$$

Besides isophthalic acid, there is always likewise formed a large quantity of benzoic acid. Chlorbenzoic acid treated in the same way yields only traces of isophthalic acid, the principal product being benzoic acid.

Meyer had formerly found that chlorosalylic acid under these circumstances is completely transformed into benzoic acid; it appears therefore that it depends on the nature of the halogens contained in the benzene nucleus, whether sodium formate acts as a source for hydrogen, effecting a resubstitution, or whether it exchanges the halogen for carboxyl.

The isophthalic acid obtained by synthesis possesses all the properties of that prepared by oxidising isoxylene, with the exception that it crystallises in microscopic needles, whilst the latter forms large needles. The authors therefore prepared the methyl ether of their acid, and compared it with the methyl ether of isophthalic acid which Baeyer had obtained from mellitic acid; both substances crystallise from alcohol in long fine needles; Baeyer's ether melts at 63°—65°, and that of the authors' at 64°—65°.

C. S.

* Deut. Chem. Ges. Ber., iv, 259—262.

On the Reduction of Dibrom-amido-benzoic Acid. By E. ANGERSTEIN.*

THE author has already obtained dibromobenzoic acid† and converted this successively into dibromonitrobenzoic acid and dibromamidobenzoic acid. By treating the latter with sodium amalgam, he now finds that it becomes converted into *meta-amidobenzoic acid* (anthranilic acid).

C. E. G.

On Fluobenzoic Acid and Fluobenzene. By R. SCHMITT and H. VON GEHREN.‡

HYDROFLUORIC acid decomposes diazo-amidobenzoic acid in a manner similar to hydriodic and hydrochloric acids, fluobenzoic acid, and hydrofluo-amidobenzoic acids being formed, and nitrogen evolved.

$$C_{14}H_{11}N_3O_4 + 2HFl = C_7H_5FlO_2 + C_7H_7NO_2HFl + 2N.$$

The mixture of the two acids was gently heated in a platinum dish until it had become entirely fluid, and the evolution of nitrogen had ceased. On cooling, the crude fluobenzoic acid crystallised out, and was purified, first by treatment with animal charcoal and crystallisation from water, and finally by solution in ether, in order to separate the hydrofluo-amidobenzoic acid which remains undissolved. Fluobenzoic acid crystallises in colourless rhombic prisms very similar to benzoic acid. It volatilizes readily at 100° and melts at 182°, and solidifies at 170°. It dissolves with difficulty in cold water, but easily in hot water, alcohol and ether. It has a strong acid reaction, expels carbonic acid from the alkaline carbonates, and does not etch glass. It is soluble without decomposition in concentrated sulphuric acid and with nitric acid forms, *nitrofluo-benzoic acid.*

With the metals, fluobenzoic acid forms neutral salts, which crystallise well from their aqueous solutions. The *silver-salt*, prepared by precipitating the ammonium salt by silver nitrate, and recrystallising, forms yellow plates having the composition $C_6H_4FlCO_2Ag$. The *calcium salt* $(C_6H_4FlCO_2)_2Ca + 3H_2O$ obtained by neutralising the acid with calcium carbonate crystallises in large prisms. The *barium salt* $(C_6H_4FlCO_2)_2Ba + 4H_2O$ was prepared in a manner similar to the calcium salt. *Ethyl fluobenzoate* was obtained by saturating an alcoholic solution of the acid with dry hydrochloric acid, it crystallises, and is volatile without decomposition. Attempts to determine accurately the amount of fluorine present in these compounds were unsuccessful.

When calcium fluobenzoate was distilled with 4·3 times its weight of

* Zeitschr. f. Chem. [2], vii, 65. † Zeitschr. f. Chem. [2], v, 514.

‡ Zeitschr. f. Chem. [2], vii, 76—77, from J. pr. Chem. [2], i, 394.

calcium hydrate it was decomposed, yielding fluobenzene. After being purified by fractional distillation, it solidified to a mass of scales. The substance melts at 40°, boils at 180°—183°, and has a vapour density of 3·476. It is insoluble in water, but easily soluble in ether and alcohol. It has an odour similar to that of benzene and burns with a smoky flame. The analysis indicated the formula C_6H_5Fl.

C. E. G.

On a New Source of Paraoxybenzoic Acid. By IRA REMSEN.*

BARTH has noticed (*Ann. Ch. Pharm.* cxlviii. 30) the formation of oxybenzoic acid, by fusing potassium sulphobenzoate with potash. In attempting to prepare pure oxybenzoic acid by this process, Remsen obtained crystals melting at 210°, solidifying again at 165°, decomposing at a temperature higher than their fusing point, and of apparently the same form as those of paraoxybenzoic acid, which he therefore concludes to be identical with that substance. Slight variations in the mode of preparing the sulphobenzoic acid appeared to influence the quantity of paraoxybenzoic acid ultimately produced; the highest result was obtained from sulphobenzoic acid prepared by exposing benzoic acid to the vapour of sulphuric anhydride, treating the agglomerated mass with fuming sulphuric acid, and gently warming for a short time.

The two acids cannot be separated by fractional crystallisation, but an imperfect separation may be effected by means of basic barium paraoxybenzoate, which is difficultly soluble in water, and is precipitated by the addition of barium hydrate to the solution of the barium salts of the two acids; under these circumstances no basic barium oxybenzoate is formed.

The author is engaged in the identification of the sulpho-acid, parent of the paraoxybenzoic acid.

F. H. H.

On Bromosulphobenzoic Acid and its Derivatives. By J. ROETERS VAN LENNEP.†

Orthomonobromosulphobenzoic acid.—This acid crystallises in small delicate needles, which deliquesce when exposed to the air. It was obtained by decomposing the lead salt with sulphuretted hydrogen. *The lead salt*, $C_6H_3Br.COO.SO_2O.Pb$ $(+ 2H_2O ?)$ was prepared by boiling the crude acid with lead carbonate. It crystallises in warty masses of needles, slightly soluble in water and alcohol, and may be purified by repeated crystallisation from the latter menstruum. *The*

* Zeitschr. f. Chem. [2], vii, 81.

† Zeitschr. f. Chem. [2], vii, 67—71.

silver salt, $C_6H_3Br.CO_2.SO_3.Ag_2$, prepared from the free acid and silver carbonate, crystallises in white needles, which are difficultly soluble in water. *The copper salt*, $C_6H_3Br.CO_2.SO_3.Cu$, prepared in a similar manner, forms green warty masses of needles, which are but slightly soluble in water. The *calcium salt*, $C_6H_3Br.CO_2.SO_3.Ca + 1\frac{1}{2}H_2O$, was obtained in the following manner:—A mixture of bromobenzoic acid, melting at 152°, with a quantity of sulphuric anhydride nearly sufficient to dissolve it, was heated until it had almost ceased to give off vapours of the anhydride. The mixture, still containing a large excess of sulphuric acid, was poured into water and after separation of the unacted upon bromobenzoic acid, neutralised with chalk or milk of lime. The calcium salt forms microscopic needles, which are readily soluble in water, but dissolve with difficulty in alcohol, whether hot or cold. It can easily be obtained pure by crystallisation from the latter solvent. The *barium salt*, $C_6H_3Br.CO_2.SO_3.Ba + 2\frac{1}{2}H_2O$, obtained by neutralising the free acid with barium carbonate, crystallises in tufts of needles, which are easily soluble in water and boiling alcohol. The *magnesium salt* forms small needles, which dissolve with difficulty in hot or cold alcohol, but easily in water. The *sodium salt* forms clusters of small needles. The *acid barium salt* $(C_6H_3Br.CO_2H.SO_2O)_2Ba + H_2O$, is produced when the neutral salt is crystallised from hydrochloric acid. It crystallises better than the neutral salt in distinct but minute needles. The *acid sodium salt*, $C_6H_3Br.CO_2H.SO_3Na$, obtained in a manner similar to the acid barium salt, crystallises from alcohol in large distinct needles. The neutral *calcium salt*, when crystallised from hydrochloric acid, forms slender glistening needles.

As all these salts, and especially the neutral ones, crystallise very badly, and in close masses, they could be but imperfectly purified, and presented great difficulties in determining their water of crystallisation.

Phosphoric bromide and sodium bromosulphobenzoate. The mutual action of sodium bromosulphobenzoate and phosphorus pentabromide,

$$C_6H_3Br\left\{\begin{matrix}SO_2ONa\\COONa\end{matrix}\right. + 2PBr_3Br_2 = C_6H_3Br\left\{\begin{matrix}SO_2Br\\COBr\end{matrix}\right. + 2NaBr + 2POBr_3,$$

yielded an oil, which was washed with water to remove sodium bromide, and then boiled with water to convert the group COBr into the group COOH. Heat partly decomposed this resinous product thus, $C_6H_3Br.CO_2H.SO_2Br = C_6H_3Br_2COOH + SO_2$. It was now dissolved in soda solution, filtered from the insoluble portion, and precipitated by hydrochloric acid, when it yielded a very small quantity of an acid. Neither this acid, nor its sodium salt, could be obtained in a distinctly crystalline state from their solutions in alcohol or water, but one or

two sublimations gave the acid in slender glistening needles, melting at 182°—184°.

Thiohydrobromobenzoic acid. Hübner and Upmann have already published a preliminary notice on this acid.* Sodium bromosulphobenzoate was gently heated with two equivalents of phosphorus pentachloride and the product washed with water, whereby monobromosulphobenzoic chloride was obtained as an oil, which is quite insoluble in water. This chloride was boiled for some hours with tin and hydrochloric acid, and the acid, which appeared as an insoluble white mass, was freed from the chloride by washing with water, and repeated solution in ammonia and precipitation by hydrochloric acid. The well washed precipitate, after being dissolved in alcohol and precipitated by water, was finally purified by repeated crystallisation from alcohol. The pure acid is almost insoluble in water, very soluble in alcohol, and melts at 242°—243° (Upmann gives 254°). The *zinc salt*, $(C_6H_3Br.SHCOO)_2Zn$, is precipitated on adding zinc sulphate to a solution of the ammonium salt; it is insoluble in water. The *lead salt*, $(C_6H_3Br.SHCOO)_2Pb$, is a white precipitate, insoluble in water, prepared by adding lead acetate to a solution of the ammonium salt. The *barium salt*, $(C_6H_3Br.SHCOO)_2Ba$, forms a white precipitate, obtained by adding barium chloride to the ammonium salt. It is somewhat soluble in boiling water, and, on evaporation, separates in microscopic crystals. The *calcium salt*, like the barium salt, is a white precipitate. The *sodium salt*, after treatment with iodine, yields an acid having a melting-point of 130°. Its lead and zinc salts, $(C_6H_3Br.S.COO)_2Zn$, are white precipitates, insoluble in water.

Metathiohydrobenzoic acid. When thiohydrobromobenzoic acid was left for some weeks in contact with sodium amalgam and water, its bromine became replaced by hydrogen, and the addition of sulphuric acid to the largely diluted solution precipitated the thiohydrobenzoic acid in white flocks. As this prolonged action of hydrogen appeared to give rise to other products, it was necessary to purify the crude acid by crystallisation from alcohol, in which it is readily soluble. It is but slightly soluble in boiling water, and separates on cooling in white flocks, which have a crystalline appearance under the microscope. The lead salt is an insoluble precipitate, having the composition $(C_6H_4SH.COO)_2Pb$, or $(C_6H_4)_2S_2(CO_2)_2Pb$. The zinc salt is a precipitate, soluble in boiling water, but uncrystallisable. The ether does not crystallise.

C. E. G.

* Zeitschr. f. Chem. [2], vi, 294.

On Mellitic Acid. By A. BAEYER.*

THE acid formerly described as *isopyromellitic* acid, which was obtained by heating hydromellitic with sulphuric acid, is a mixture of two isomeric tetrabasic acids, $C_6H_2(CO_2H)_4$, which the author calls *prehnitic* and *mellophanic acid.*

Prehnitic acid is readily soluble in water, and crystallises from its concentrated solution in large prisms, which resemble the mineral prehnite. They contain 2 mol. water of crystallisation, which escape on heating; the anhydrous acid melts at 237°—250°, with formation of the anhydride; the fused mass solidifies quickly at 220° into a crystalline mass, which resembles sal-ammoniac, and melts again at 239°. The aqueous solution of the acid gives with barium chloride a precipitate of small octohedral crystals, having the composition $(C_{10}O_8H_5)_2Ba$, and containing 3 or 4 mol. water of crystallisation. The methyl-ether of prehnitic acid crystallises in small thick concentrically-grouped prisms, which melt at 104°—108°, solidify at 81°—70°, and sublime without decomposition. By the action of sodium amalgam, the acid is converted into hydroprehnitic acid, a syrupy liquid, which on heating yields isophthalic acid, besides regenerated prehnitic acid.

Mellophanic acid, which is also readily soluble in water, forms crystalline crusts; it is anhydrous. From a solution containing a little hydrochloric acid it crystallises in fine prisms. Its aqueous solution is not precipitated by barium chloride. At 215° it begins to soften and shrink together, and at 238° it forms a clear liquid containing the anhydride, which on cooling solidifies into crystals resembling frost-flowers and melting at 164°.

If the action of sulphuric acid on hydromellitic acid has not been carried on too long, there is also a third acid formed in varying quantities, as by the further action of hot sulphuric acid it is converted into prehnitic acid. This acid, called *prehnomalic acid*, $C_{10}H_8O_9$,† is tetrabasic; if its aqueous solution is evaporated on the water-bath an amorphous mass, $C_{20}H_{14}O_{17}$, is left behind, which is very soluble in water; this solution soon solidifies to a magma of bulky needles, having the composition $C_{20}H_{14}O_{17} + 4H_2O$, and only sparingly soluble.

Prehnomalic acid has the composition of prehnitic acid + water, and is easily transformed into the latter acid; this change is effected not only by hot sulphuric acid, but also by bromine-water, and, what is still more singular, by the action of methylic iodide upon the silver-salt, the methyl-ether of prehnitic acid being formed.

* Deut. Chem. Ges. Ber., iv, 273—278.

† Formerly described as mesohydromellitic acid, with the incorrect formula $C_{12}H_{12}O_{12}$.

Prehnomalic acid corresponds to Otto's oxyhydrobenzoic acid—

$$\underset{\text{Oxyhydrobenzoic acid.}}{2[C_6H_8(OH).CO_2H]} - H_2O = \underset{\text{Hydroxydibenzoic acid.}}{HO_2C.C_6H_8.O.C_6H_8.CO_2H.}$$

$$\underset{\text{Prehnomalic acid.}}{2[C_6H_3(OH)(CO_2H)_4]} - H_2O = \underset{\text{Acid dried at 100°.}}{(HO_2C)_4C_6H_3.O.C_6H_3(CO_2H)_4.}$$

Prehnomalic acid dried at 100° melts at 210°, with loss of water, to a colourless liquid; at a higher temperature it distils; and the distillate solidifies to a varnish-like mass, which melts at 180°.

We are now acquainted with all the carbon acids of benzene (except the pentabasic acid) which, according to Kekulé's theory, can exist—

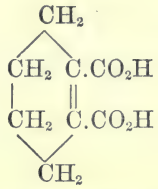
$C_6(CO_2H)_6$.	Mellitic acid.		
$C_6H_2(CO_2H)_4$.	Pyromellitic acid.	Prehnitic acid.	Mellophanic acid.
$C_6H_3(CO_2H)_3$.	Trimellitic acid.	Trimesic acid.	Hemimellitic acid.
$C_6H_4(CO_2H)_2$.	Terephthalic acid.	Isophthalic acid.	Phthalic acid.
$C_6H_5(CO_2H)$.	Benzoic acid.		

When hydropyromellitic acid is distilled, *tetrahydrophthalic anhydride* $C_8H_8O_3$ comes over,—a white foliated mass, insoluble in water, and crystallising from ether in hard shining plates. On boiling it with water, it is converted into the bibasic *tetrahydrophthalic acid* $C_8H_{10}O_4$, which is very soluble, and crystallises in plates. It melts at 96°, being again transformed in the anhydride. By the action of sodium amalgam or concentrated hydriodic acid it is converted into *hexahydrophthalic acid* $C_8H_{12}O_4$, which forms small indistinct, hard crystals. This is also bibasic and melts at 203°—205°, solidifying again in needles.

This acid is a derivative of benzene, and contains the carbon atoms still linked together in a ring: for if the connection between two atoms had been broken, suberic acid would have been formed, which contains two atoms of hydrogen more, and in which the carbon atoms form an open chain. We have, therefore, the following series:—

	Suberic acid	$C_8H_{14}O_4$.
Derivatives of benzene.	Hexahydrophthalic acid ..	$C_8H_{12}O_4$.
	Tetrahydrophthalic acid ..	$C_8H_{10}O_4$.
	Hydrophthalic acid	$C_8H_8O_4$.
	Phthalic acid	$C_8H_6O_4$.

As tetrahydrophthalic acid is so easily converted in its anhydride, it appears most probable that the two carboxyl groups are combined with two adjoining carbon atoms, just as in phthalic acid, and that the four other carbon atoms are each combined with two atoms of hydrogen, its constitution being as follows:—



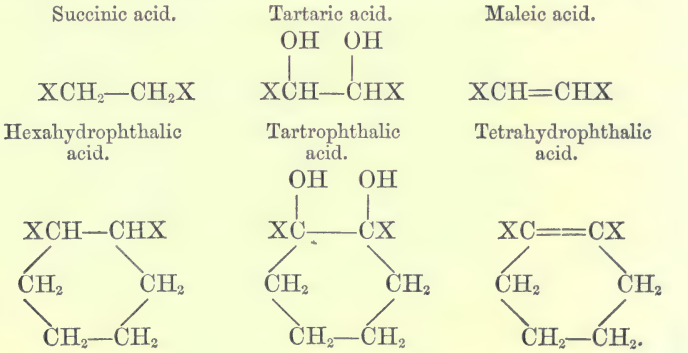
When bromine is added to its aqueous solution, *bromo-malophthalic acid* $C_8H_{10}Br(OH)O_4$ is formed, which crystallises in hard, white crusts. This body bears the same relation to tetrahydrophthalic acid as bromo-malic acid bears to maleïc acid—

$$\underset{\text{Maleïc acid.}}{C_4H_4O_4} + BrOH = \underset{\text{Bromo-malic acid.}}{C_4H_4Br(OH)O_4}.$$

$$\underset{\text{Tetrahydrophthalic acid.}}{C_8H_{10}O_4} + BrOH = \underset{\text{Bromo-malophthalic acid.}}{C_8H_{10}Br(OH)O_4}.$$

This bromo-acid is readily soluble in water; when it is heated with baryta-water, the barium salt of *tartrophthalic acid* $C_8H_{10}(OH)_2O_4$ is formed. This acid is bibasic, very soluble, and crystallises in fine large prisms.

It is thus seen that hexahydrophthalic acid forms derivatives analogous to those of succinic acid, and the constitution of the two series, which are connected by a peculiar kind of homology, is expressed by the following formulæ, in which X represents CO_2H—



C. S.

On a Derivative of Gallic Acid. By G. Rembold.*

In the preparation of ellagic acid according to Löwe's process, by heating gallic acid to 120° with arsenic acid, if the product insoluble in

* Zeitschr. f. Chem. [2], vii, 60, from Ann. Ch. Pharm., clvi, 116.

water, and consisting chiefly of ellagic acid, be treated with sodium amalgam, then acidified, filtered, and agitated with ether, several substances are obtained, distinguished from one another by the difference of their solubility in water.

Amongst these is a substance, $C_{14}H_{10}O_7$, consisting of pale greenish-yellow, glistening needles, which are soluble with difficulty in cold water, and with calcium hypochlorite become first dirty violet, then brown, and finally almost colourless; with ferric chloride greenish-blue, then green, and on the addition of soda, greenish-brown; with ammonia they become brown; with silver nitrate, brownish-black from reduced silver; and with nitric acid, yellowish. Concentrated sulphuric acid partially dissolves them with a yellow colour. Manganese peroxide and concentrated sulphuric acid give a fine purple-red. The substance is a weak acid, and its salts with the alkaline earths oxidise quickly in the air; a crystalline barium salt, however, appears to be formed by treating it with barium carbonate in a current of hydrogen. Occasionally another crystalline substance, probably $C_{12}H_{10}O_8$, is obtained, which is also a weak acid, and but slightly soluble in water; it becomes red by treatment with ferric chloride. Amongst the products which are more soluble in water, and redden litmus strongly, is found a substance crystallising in plates, which give a bluish-green reaction with iron chloride. C. E. G.

On an Aromatic Glycollic Acid. By W. Dittmar and Aug. Kekule.*

The toluic acid employed for the preparation of this acid is the one corresponding to terephthalic (paraphthalic) acid, and is readily obtained in the pure state from cymene. This hydrocarbon, which can be easily prepared in quantity from camphor, yields, when slowly oxidized, only one of the three known toluic acids, and by a more powerful oxidation, terephthalic acid. The preparation from dimethyl-benzene obtained synthetically from solid bromotoluene is evidently more difficult. The xylene from coal-oil is a mixture of tere-xylene (para-xylene) and iso-xylene (metaxylene) and gives by oxidation much isotoluic (metaloluic) acid, and but little teretolylic (paratoluic) acid; and although the former could be separated in the pure state, the authors were unable to obtain any quantity of the latter sufficiently pure. The cymene employed is prepared from camphor by means of phosphorus sulphide, and oxidized by long boiling with dilute nitric acid, whereby toluic and some nitrotoluic acids are formed, and generally a little terephthalic acid. As a considerable quantity of acetic acid is produced at the same time, it may be inferred that this cymene contains normal propyl, and not isopropyl. The separation of the toluic acid from the terephthalic

* Zeitschr. f. Chem. [2], vii, 56, from Deut. Chem. Ges. Ber., iii, 894.

acid is easily effected by dissolving it in ether, evaporating, and distilling the acid over with the vapours of water.

After several unsatisfactory attempts to obtain the chloromethyl-phenyl-formic acid, the authors turned their attention to the corresponding bromine-compound, which they prepared by heating toluic acid to 160° to 170° in a long-necked retort, and passing slowly over it, by means of a water aspirator, the vapour of rather more than the theoretical quantity of bromine: owing to the difficulty of purifying it, the authors have not yet investigated this acid. In order to obtain the oxy-acid from this crude product, it is boiled with baryta-water, when the bromine in it is replaced by hydroxyl. *Oxy-methyl-phenylformic acid* crystallises in plates or flat needles, is very soluble in hot water, and even in the cold far more soluble than toluic acid; it is soluble in ether. Its melting-point is somewhat higher than that of toluic acid, and it sublimes in feathery needles.

The analyses of the acid lead to the formula $C_6H_4.CH_2.OH.COOH$, which was confirmed by an analysis of the silver salt.

C. E. G.

II. *Researches on the Sulpho-acids of the Mesitylenes.* By H. Rose.*

Nitrosulphomesitylenic acid from sulphomesitylenic acid. Sulphomesitylenic acid was gradually added to carefully cooled fuming nitric acid, whereupon it dissolved, forming a deep brown solution, which after a few hours became almost colourless. This was now poured into a large quantity of water, filtered from the white flocks of dinitromesitylene which separated along with a small quantity of an oil, probably impure nitromesitylene, and repeatedly evaporated at 100° with the addition of water, in order to remove the excess of nitric acid. The crystalline mass, after being pressed and recrystallised, readily yielded the pure acid in brittle, transparent, prismatic crystals. *Nitrosulphomesitylenic acid*, $C_6(CH_3)_3HNO_2SO_3H + 1\frac{1}{2}H_2O$, is easily soluble in water, alcohol, and ether, and melts at 131°. Exposure to sunlight turns it yellow, and when dried over sulphuric acid it becomes opaque, and loses its water of crystallisation. Most of its salts are easily soluble in water, crystallise well, and burn with deflagration.

The *barium salt*, $[C_6(CH_3)_3HNO_2SO_3]_2Ba$, crystallises from its hot aqueous solution in pale yellow tufts of crystals. It is almost insoluble in ether, soluble with difficulty in cold water and in alcohol. The *potassium salt*, $C_6(CH_3)_3HNO_2SO_3K + H_2O$, forms large white needles or broad plates, and is readily soluble in alcohol and water. The *copper salt*, $[C_6(CH_3)_3HNO_2SO_3]_2Cu + 3H_2O$, crystallises in pale green lustrous scales, which are tolerably soluble in cold water. The *lead*

* Zeitschr. f. Chem. [2], vii, 74—76.

salt, $[C_6(CH_3)_3HNO_2SO_3]_2Pb + H_2O$, is easily soluble in water, and crystallises from its hot solutions in white glistening tufts of needles. The *ammonium salt* is readily soluble in alcohol and water, and separates in nodular concretions.

Amidosulphomesitylenic acid, $C_6(CH_3)_3HNH_2SO_3H + H_2O$, was prepared from the nitro-acid by dissolving it in ammonia, saturating the solution with sulphuretted hydrogen, and evaporating it almost to dryness; water was then added, and the boiling solution decomposed by hydrochloric acid. The filtered solution, on cooling, deposited the amidosulphomesitylenic acid in the form of pale red needles, which were rendered white by treatment with animal charcoal and recrystallisation. The acid is easily soluble in hot alcohol, with difficulty in cold water, but much more readily in hot. By slowly cooling its aqueous solution, it can be obtained in fine truncated prisms, and from a hot concentrated solution, in needles, which acquire a red tinge on exposure to light. It loses its water of crystallisation when dried over sulphuric acid. It does not combine with hydrochloric acid, and crystallises unchanged from moderately strong sulphuric acid. Its solutions redden litmus-paper, and it expels carbonic acid from the carbonates.

Its salts crystallise well, and are generally, easily soluble; their solutions become yellow on evaporation from incipient decomposition. The *barium salt*, $[C_6(CH_3)_3HNH_2SO_3]_2Ba$, crystallises from its hot aqueous solution in yellow nodules, which are tolerably soluble in cold water. The *magnesium salt*, $[C_6(CH_3)_3HNH_2SO_3]_2Mg + 3H_2O$, forms hard transparent crystals of a yellow colour. The *zinc salt*, $[C_6(CH_3)_3HNH_2SO_3]_2Zn + 5H_2O$, is readily obtained in fine crystals, which are easily soluble in cold water. The *lead salt*, $[C_6(CH_3)_3HNH_2SO_3]_2Pb + H_2O$ is also readily soluble in cold water, and crystallises well. The *calcium, sodium, and ammonium salts* are also readily soluble in cold water, the *silver salt* much less so.

The author's endeavours to prepare *nitrosulphomesitylenic acid directly from nitromesitylene* have hitherto been unsuccessful.

C. E. G.

On Sulphanilic Acid. By E. Ador and Victor Meyer.*

Although in many cases Kekulé's prevision of the mutual repulsion of similar groups in benzene derivatives has been established, yet the production of a crystallised dibromobenzenel (1 : 4), together with a fluid isomeride and other analogous cases of isomerism, induced the authors to endeavour to show the position of the lateral chains in some benzene derivatives by the introduction into the benzene of diversely functioned

* Deut. Chem. Ges. Ber., iv, 5—10.

groups, anticipating thereby an intimate juxtaposition of the lateral chains, Meyer having shown* that Cl, Br, I or NO_2, when introduced into aromatic amines, steps in by the side of the amidogen group, in consequence of the attraction of the positive NH_2 group for the negative substituted group.

Sulphanilic acid appeared to offer unusual facilities for ascertaining the relation of the SO_3H group to the amidogen group, for it would seem, more than any other substance, to call for the assumption that the lateral chains lie close to one another.

The acid was prepared by gradually adding 1 pt. of aniline to 2 pts. of fuming sulphuric acid, repeatedly crystallising from boiling water, and purifying with animal charcoal. The diazo-derivative of the acid was treated with hydrobromic acid, giving bromobenzene sulphuric acid, which by distillation of its potassium salt with potassium cyanide, gives terephthalic acid.†

Terephthalic acid has the constitution represented by 1 : 4, and the same might perhaps be said of its source, sulphanilic acid, but it seemed more probable that the latter, and also bromobenzene-sulphuric acid, possessed the constitution 1 : 2, and that during distillation a rearrangement had occurred, resulting in the order 1 : 4.

To examine this point further, the potassic bromobenzene-sulphate was fused with twice its weight of potash, the product dissolved in water, acidified, sulphurous acid boiled off, and the cold solution shaken with ether; the ethereal solution gave on evaporation a brown syrup, which was dissolved in water, filtered, evaporated, and exposed over quicklime. The product was distilled and passed over in large plates of pure resorcin, fusing at 105°. The same substance was likewise obtained from phenolsulphuric acid (produced by boiling the before-mentioned diazo-compound with water), by fusing it with potash.

Resorcin has the same constitution 1 : 4 as terephthalic acid; therefore sulphanilic acid holds the sulpho- and amide-groups in the positions 1 : 4, and the law of the distribution of substituted Cl, Br, I, and NO_2 does not extend to the complex sulpho-group; it follows that the brombenzene-sulphuric acid obtained from sulphanilic acid, shares with it the 1 : 4 arrangement, and is identical with Couper's acid; whilst Schmitt's phenolsulphuric acid, produced by boiling the diazo-derivative of sulphanilic acid with water, is identical with Kekulé's (1 : 4) phenol-parasulphuric acid.

On the other hand, the oxidation of repeatedly purified sulphanilic acid by potassium di-chromate and sulphuric acid gave rise to a yellow substance, extremely like quinone, both in odour and in other properties, save that it melts at 66° instead of 115°; treated with sulphur-

* V. Meyer, Ann. Ch. Pharm., clvi, 286.

† Ann. Ch. Pharm., clvi, 292.

dioxide it gave inodorous white crystalline crusts of hydroquinone, which, when oxidised, gave quinone, melting at 111° instead of 115° (probably from traces of impurities).

This substance could not be obtained from toluidine, and therefore was not a toluquinone produced from toluidine present in the aniline used.

The authors are unable to explain this phenomenon, but point to the fact observed by Hofmann, that by the oxidation of β-phenylenediamine (belonging to the 1 : 2 order) quinone is produced, whilst α-phenylenediamine obtained from di-nitro-benzene having the structure 1 : 4, gave by oxidation recognisable, though minute quantities of quinone.

F. H. H.

On the action of Sulphuric Acid on Opianic Acid. By C. LIEBERMANN and C. CHOJNACKI.*

ANDERSON, in 1856, by heating together sulphuric and opianic acids, obtained a compound which gave with iron or alumina mordant, colours resembling those produced by madder. Anderson not having returned to the subject, the authors have endeavoured to throw some light on the nature of this colouring matter.

They obtain it by heating opianic acid with 30 times its weight of sulphuric acid to 180°; the liquid becoming violet red. The liquid is poured into water, and the black flocks separated are dissolved in solution of soda, and precipitated therefrom by an acid. The precipitate is dissolved in ether, and from this solution the colouring matter is obtained in yellowish-red crusts, which are purified by frequent repetition of the whole of the above-mentioned process.

It gave, on distillation with zinc powder, a colourless sublimate, which was recognised by its reactions as anthracene. Its solution in alkali has the colour of purpurin; it is, however, distinguished from purpurin and alizarin by the violet-red colour of its solution in concentrated sulphuric acid. This latter property is shared by rufigallic acid, from which, nevertheless, the new body differs in some of its properties. It gives coloured precipitates with lead and barium solutions, and produces with mordants, colours, resembling more those obtained with rufigallic acid than with alizarin. The analysis of the substance gave the following numbers :—

	I. Dried at 125°.	II. Dried at 140°.	$C_{14}H_8O_6$. Requires.
C	62·2	62·6	61·7
H	4·1	3·8	3·0

* Deut. Chem. Ges. Ber., iv, 194.

The authors believe that $C_{14}H_8O_6$ does not express the composition of the body, but reserve decision on this point.

Oxysalicylic acid, $C_7H_6O_4$, when heated rather strongly with sulphuric acid, is decomposed, with evolution of gas. W. H. D.

On Anthraflavic Acid. By EDWARD SCHUNCK, PhD., F.R.S.*

ARTIFICIAL alizarin, as prepared from anthracene by the method discovered by Gräbe and Liebermann is, according to the author, always accompanied by other substances, some of which are coloured, while others are colourless, or nearly so. One of these substances, separated in the form of yellow silky needles, has been named by the author anthraflavic acid, to indicate its origin and its most obvious external property. This body is but a feeble acid, although it yields with bases compounds of well defined character, some of which are regularly crystallised. All the compounds of this acid which are soluble in water yield yellow solutions, but it possesses no dyeing properties. It is chiefly the presence of anthraflavic acid in crude alizarin that affects the colour of the alkaline solution, changing the violet due to alizarin into purple, or when present in larger quantity, into red. For the same reason an alkaline solution of crude alizarin does not show the absorption-bands in the spectrum so distinctly as one of pure alizarin. Alkaline, as well as alcoholic solutions of anthraflavic acid, absorb the blue end of the spectrum very powerfully, though no bands are visible, even with very dilute solutions. A solution of the acid in concentrated sulphuric acid, if not too dark, shows, however, a broad but well-defined absorption-band at the extreme edge of the blue, bordering on the green, accompanied by a total absorption of the violet, as seen with the other solutions.

Anthraflavic acid is bibasic, and its composition is expressed by the formula $C_{15}H_{10}O_4$. Though it is very different in properties from alizarin, a very simple experiment is sufficient to prove that the two are very closely related. When pure anthraflavic acid is dissolved in an excess of caustic potash, and the solution is boiled down to dryness, a yellow residue is left, which, after being carefully heated almost to fusion, dissolves in water with a red colour; this solution contains alizarin.

Anthraflavic acid, like alizarin, appears to be reduced to anthracene by zinc powder. J. B.

On the Preparation and Analysis of Sericic and Lanuginic Acids. By P. CHAMPION.

Sericic Acid. Purified silk heated with a concentrated solution of baryta to ebullition is partially dissolved. If the liquid be then filtered, the

* Chem. News, xxiii, 157.

excess of baryta removed by carbonic acid, and a solution of lead nitrate added, a heavy precipitate is formed. This precipitate washed and treated with sulphuretted hydrogen yields, on evaporation to dryness, sericic acid in the form of a yellowish, translucent uncrystallisable mass, which is deliquescent and soluble in alcohol and acetic acid. Its barium salt gave by analysis 39·5 p. c. C., 6·2 H., 13·0 N., 26·2 O., and 15·1 Ba., which numbers give for sericic acid, the empirical formula, $C_{30}H_{60}N_8O_{14}$.

Lanuginic Acid may be obtained by operating in the same way upon purified wool. Its appearance and properties are similar to those of sericic acid. The percentage composition of barium lanuginate has been found to be 40·8 C., 5·4 H., 12·8 N., 28·7 O., and 12·3 Ba., giving for lanuginic acid the empirical formula $C_{38}H_{60}N_{10}O_{20}$.

J. B.

Some Reactions of Cholic Acid. By E. von Gorup-Bezanez.*

1. *Action of Phosphorous Chloride on Cholic Acid*, $C_{24}H_{40}O_5$.—By dissolving powdered cholic acid in phosphorous chloride, much hydrochloric acid was evolved, and a thickish fluid was obtained, from which the addition of water precipitated a white resinous mass. When heated with water to boiling, this mass melts and forms on cooling an easily pulverizable lump. This was purified by boiling it with successive portions of water till they no longer acquired an acid reaction, dissolving it in warm carbonate of soda, and precipitating it by hydrochloric acid, repeating this several times, and finally treating it with ether. The product proved to be a peculiar acid containing phosphorus. When dry it presented the appearance of a fine dusty white powder which, on microscopic examination, was seen to consist of highly refracting granules without any trace of crystals.

It had a slightly bitter taste, no smell, was insoluble in water either cold or boiling, soluble in alcohol and chloroform, sparingly soluble in ether. When heated on platinum foil it melted, became brown, took fire and burned with a greenish flame and emission of thick white fumes, leaving a cinder which burned with difficulty and had a strong acid reaction, from phosphoric acid. It gave Pettenkofer's reaction with sugar and sulphuric acid.

The numbers obtained from analyses of different portions of the acid nearly correspond to the empirical formula $C_{72}H_{114}P_2O_{15}$. If this formula were correct the reaction might be—

$$3C_{24}H_{40}O_5 + 2PCl_3 = C_{72}H_{114}P_2O_{15} + 6HCl.$$

Unfortunately, however, we have no guarantee for the purity of the acid, as neither it nor its salts can be obtained in the crystalline state.

* Ann. Ch. Pharm., clvii, 282—285.

This difficulty prevented the author from pursuing the research further, although the probable formation of this body by the union of three molecules of cholic acid is of extreme interest, when considered in connection with the extraordinary high molecular weight by which all the components of brain and nerve containing phosphorus at present known are distinguished.

It would appear that with the entrance of tri- or quinquivalent phosphorus, several molecules of compounds free from phosphorus may unite to form a condensed molecule containing phosphorus.

Another very interesting product is obtained by treating cholesterin with phosphorous chloride. It is a neutral body, containing phosphorus, but unfortunately very difficult to purify. In water it swells up like starch-paste, and resembles in this property the so-called myelin of Virchow.

2. *Action of melting Caustic Potash on Cholic Acid.*—Lehmann states in his Handbook of Physiological Chemistry (1859, 69), that cholic acid when treated with melting caustic potash yields palmitic, propionic, acetic, and formic acids. He assumes this to be a well authenticated fact, infers from it the subsistence of a close relation between cholic and oleic acids, and founds upon it a hypothesis as to the formation of bile-acids in the organism. It seems, however, that this statement has not been confirmed by any one, and on submitting it to the test of experiment, Gorup-Bezanez found that propionic and acetic acids were produced, but neither palmitic nor formic acid.

At his desire the experiments were repeated by Dr. H. Rosshirt, who obtained the same result and found propionic and acetic acid in nearly equal proportions.

A great portion of the cholic acid was also found to be converted during the experiment into an amorphous brown resin which was brittle when cool, presented the characters of *Dyslysin*, and was extremely indifferent to chemical reagents.

T. L. B.

An improved Method of obtaining Glycocholic Acid. By. E. v. Gorup-Bezanez.*

The author finds that the following method of obtaining glycocholic acid is easier and more certain, and yields a larger amount of acid than those of Strecker or Hoppe-Seyler.

Ox gall is taken from the bladder, evaporated nearly to dryness in a water-bath, and the residue is exhausted with alcohol of 90 per cent. The alcohol is evaporated or distilled off; the residue, diluted if necessary with water, is treated with milk of lime and gently warmed,

* Ann. Chem. Pharm., clvii, 286, 287.

whereupon the greater part of the colouring matter is carried down with the lime, and the liquid is filtered and allowed to cool.

The filtrate, generally of a slight wine-yellow colour, is then treated with dilute sulphuric acid (avoiding excess) till a permanent turbidity is produced and allowed to stand. In a few hours the whole fluid becomes a mass of crystals of glycocholic acid.

This is thrown on a filter (it is best filtered by using a water air-pump), washed with cold water and pressed, first between blotting-paper and then in a wooden screw press. The acid is then generally colourless. It may be further purified by again dissolving it in a large amount of lime-water and adding dilute sulphuric acid till a permanent turbidity is produced when perfectly pure glycocholic acid separates in fine needles of dazzling whiteness.

Hoppe-Seyler allows the alcoholic solution of the acid to evaporate at ordinary temperatures, and the acid to recrystallise from this in order to purify it.

Gorup-Bezanez, like Strecker, could never obtain crystals in this way, but always got a resinous mass. By his own method it sometimes happens that several hours after a permanent turbidity has been produced in the filtrate from the lime precipitate by dilute sulphuric acid, a thickish oily mass is found at the bottom of the vessel while the liquid above becomes gradually clear. After a few days or weeks, this mass becomes converted into crystals of glycocholic acid. What conditions occasion this anomaly he was unable to discover.

T. L. B.

On a Compound of Aldehyde and Sulphaldehyde. By A. Pinner.*

The author finds that the oil produced by passing sulphuretted hydrogen through aqueous aldehyde, has the composition $C_2H_4O + C_2H_4S$.

This body solidifies at —8° C., and melts at —2° C.; it cannot be distilled without decomposition. On treatment with an acid, solid sulphur aldehyde is precipitated, and aldehyde goes into solution. No sulphuretted hydrogen is evolved in this latter reaction.

The author's results directly contradict those of Weidenbusch, who obtained, under these circumstances, an oil having the composition $6(C_2H_4S) + SH_2$, and yielding sulphuretted hydrogen on treating with an acid. Repeated efforts made by the author failed to yield this oil. He invariably obtained the above-mentioned compound.

E. T. C.

* Deut. Chem. Ges. Ber., iv, 257, 258.

Preparation of Acetochloral from Aldehyde. By A. PINNER.*

THE author, in conjunction with Krämer, had previously been studying the action of chlorine on aldehyde; they then found a new chloral bearing the same relation to crotonic aldehyde that acetochloral bears to common aldehyde.

The cause of this became apparent on the publication of Kekulé's research on crotonic aldehyde. For by the action of chlorine on aldehyde, anhydrous hydrochloric acid would be generated; and this, by taking water from two molecules of aldehyde, produced crotonic aldehyde, which then became the point of attack for the chlorine: hence the production of the new chloral.

With a view to eliminating the hydrochloric acid as fast as it was formed, the author added fragments of marble to moist aldehyde, and passed a slow stream of chlorine over it; the marble was not attacked when the aldehyde was dry. At first, the aldehyde was cooled with ice, but shortly the temperature could be raised, until at last the operation was carried on at 100° C. By reason of the presence of water, the greater proportion of the aldehyde was oxidised; still, 50 grm. of aldehyde yielded by this treatment 15 to 20 grm. of a distillate which presented all the characteristics of acetochloral. The author proves conclusively that the body in hand was slightly impure chloral.

E. T. C.

On the Action of Nascent Hydrogen (from Sodium-Amalgam) on Bitter-Almond Oil. By HUGO AMNANN.†

THE following notes are contributed by R. Fittig, from the memoranda of the author who was killed in the late war.

By the action of sodium-amalgam on bitter-almond oil in aqueous or alcoholic solution, there are formed, besides benzyl alcohol, two isomeric compounds, the one identical with Zinin's hydrobenzoïn, whilst the other may be named isohydrobenzoïn. The latter is the principal product of the action of sodium-amalgam on bitter-almond oil in presence of warm water; both isomerides are obtained if an alcoholic solution be used, the proportion of hydrobenzoïn rising with the strength of the alcohol employed. Their separation is very difficult, and can only be effected by repeated crystallisation from alcohol, in which isohydrobenzoïn is somewhat the more soluble.

Hydrobenzoïn crystallises from water and alcohol in anhydrous silky scales, soluble in 80 p. water at 100° and 400 p. water at 15°, easily soluble in alcohol, fusible at 132·5°.

* Deut. Chem. Ges. Ber., iv, 256, 257.

† Zeitschr. f. Chem. [2], vii, 83.

Isohydrobenzoïn crystallises from water in hydrated brilliant needles, from alcohol in well defined hexagonal crystals. It dissolves in 80 p. water at 100° and 526 p. water at 15°, is easily soluble in alcohol, and melts at 119·5°. It is unaltered by eight days' digestion in alcoholic solution with sodium-amalgam, and therefore seems to be not convertible into benzyl alcohol.

The analyses of both substances agree with the formula $C_{14}H_{14}O_2$.

Action of Acetyl Chloride.—After 24 hours' digestion with acetyl chloride and expulsion of the excess by a current of air, both substances yielded products corresponding to the formula $C_{14}H_{12}(OC_2H_3O)_2$; the isohydrobenzoïn derivative could only, with extreme difficulty, be obtained in crystals, which melted at 117°—118°; this substance seems to be identical with the acetic ether obtained by Limpricht and Schwanert from stilbene bromide (which melts at 105°—120°).

Action of Nitric Acid.—Zinin found that hydrobenzoïn is easily converted into benzoïn by nitric acid. Isohydrobenzoïn dissolves readily in this reagent; the product of the reaction collects on the surface of the liquid in oily drops, which in contact with water pass into a tough yellow mass, which could not be made to yield any definite compound suitable for analysis.

Action of Phosphoric Chloride.—The reaction with isohydrobenzoïn seems to be more energetic than with hydrobenzoïn. The product of the reaction was the same with both substances, was very sparingly soluble in alcohol, and crystallised from toluol in colourless needles, melting at 184°, and having the composition $C_{14}H_{12}Cl_2$.

F. H. H.

On the Distillation-products of a Mixture of Butyrate and Acetate of Calcium. By Ferdinand Grimm.*

An intimate mixture of equal molecules of butyrate and acetate of calcium was heated in glass retorts coated with clay. A brown liquid distilled over, whilst gases escaped, amongst which was propylene. From the liquid, which began to boil at 60°, the boiling-point rising at the end to 320°, no definite products could be obtained by fractional distillation. The portion boiling between 85° and 120° was therefore shaken with a concentrated solution of sodium bisulphite; the crystals thus obtained were decomposed with sodium carbonate, and the acetone set free was again combined with the sulphite and again set free. From this liquid by repeated fractional distillation a body was isolated, boiling constantly at 99°—101°, and having the composition $C_5H_{10}O$, which according to its properties and mode of formation must be *propyl-methyl ketone*, $CO\left\{\begin{matrix}C_3H_7\\CH_3\end{matrix}\right.$. It is a colourless mobile liquid,

* Ann. Ch. Pharm., clvii, 249—264.

having a high refractive power and a smell like acetone; with alkaline bisulphites it forms compounds which crystallise well. The sodium salt has the composition $C_5H_9NaSO_3 + 1\frac{1}{2}H_2O$. By treating the ketone with water and metallic sodium, *secondary amyl alcohol*, boiling at 118°—120°*, and *propyl-methyl pinakone*, $C_{10}H_{22}O_2$, boiling at 225°—230°, were formed.

These results do not agree with those of Limpricht and v. Uslar, who distilled the barium salt of the so-called butyro-acetic acid, and obtained, besides other bodies, a compound having the composition $C_5H_{10}O$, which they call *propione*, but which boils at 110°. Friedel, who studied also the distillation-products of a mixture of calcium butyrate and acetate, obtained, together with other products, a liquid boiling at 111°, which he calls methyl-butyryl, $CH_3.C_4H_7O$. It appears most probable that these bodies were nothing but impure propyl methyl-ketone, as Limpricht and v. Uslar found too little carbon, and Friedel on treating his substance with nascent hydrogen obtained a secondary alcohol boiling at 120°—123°, and a pinakone boiling at 220°—225°. Propyl-methyl ketone is no doubt identical with Frankland and Duppa's ethylated acetone, which boils at 101°, for "ethylated methyl" is identical with "propyl."

Ethylated acetone. $O\left\{\begin{matrix} CH_2.C_2H_5 \\ CH_3 \end{matrix}\right.$

Propyl-methyl ketone. $CO\left\{\begin{matrix} C_3H_7 \\ CH_3. \end{matrix}\right.$

From the distillation products boiling below 100°, the author isolated by fractional distillation a liquid boiling at 77°—79°, and having the composition C_4H_8O. This body possesses all the properties of *ethyl-methyl ketone*, $CO(C_2H_5)(CH_3)$, which was first discovered by Fittig in commercial acetone, and afterwards prepared synthetically by Freund, who obtained it by acting upon zinc-ethyl with acetyl chloride, and by Popoff, who showed that the same body is obtained from zinc-methyl and propionyl chloride; both yield by oxidation only acetic acid. The same acid was obtained by the author on oxidising his compound.

Besides these two ketones, dimethyl ketone (common acetone) and dipropyl ketone were formed; this was to be expected, as these two compounds are formed by distilling each of the two calcium salts separately. The *propylal*, C_3H_6O, described by Limpricht and v. Uslar, which boiled at 66°, was most likely a mixture of moist dimethyl and ethyl-methyl ketone.

Dipropyl ketone, $CO(C_3H_7)_2$, (butyrone) forms, according to Limpricht, crystalline compounds with the alkaline bisulphites. The author doubted the correctness of this statement, as he had formerly

* This alcohol must be identical with that prepared by Wurtz from isoamylene (ethyl-allyl).—C. S.

found that only such ketones in which one of the alcohol-radicals is *methyl* have this property; thus, besides the ketones mentioned above, also methyl-butyl ketone, methyl-caproyl ketone, and methyl-nonyl ketone combine readily with bisulphites, whilst diethyl ketone, propyl-ethyl ketone, and dibutyl ketone do not possess this property.

The dipropyl ketone which the author obtained boiled at 143°—146°, and had all the properties of this body, as they are stated in handbooks. It was shaken with a concentrated solution of sodium bisulphite, and the mixture allowed to stand for a week in a cool place. Another portion was treated in the same way with ammonium bisulphite; but in neither of the liquids did either crystals or an oily compound separate out. It is remarkable that Frankland and Duppa's *diethylated acetone*, $CO\left\{\begin{matrix}CH(C_2H_5)_2\\CH_3\end{matrix}\right.$, forms only an oily compound with sodium bisulphite. C. S.

Synthesis of Rue-oil. By E. von Gorup-Bezanez and F. Grimm.*

This compound was regarded for a long time as an aldehyde. According to Strecker, however, it is *nonyl-methyl ketone*, $CO\left\{\begin{matrix}C_9H_{19}\\CH_3\end{matrix}\right.$; but the correctness of this view has not hitherto been fully proved by experiment, which could only be done by obtaining this compound synthetically. The authors, therefore, prepared this ketone, in order to compare its properties with those of rue-oil. They obtained it by distilling a mixture of equal molecules of caprate and acetate of calcium:—

$$(C_9H_{19}CO)_2CaO_2 + (CH_3CO)_2CaO_2 = 2CO(C_9H_{19})(CH_3 + 2CaCO).$$

The distillate consisted of a liquid boiling below 200°, another boiling between 210°—245°, and solid caprone (*vide* preceding paper). The liquid boiling between 210°—245° was dissolved in alcoholic ammonia, and the solution saturated with sulphurous acid gas. On cooling, the double compound crystallises in white pearly plates, which can be recrystallised from hot alcohol; its composition is $C_{11}H_{22}O.NH_4SO_3 + H_2O$. By heating it with a dilute solution of sodium carbonate, the ketone separates as a light colourless oil, which has a high refractive power, and the characteristic smell of rue. Its sp. gr. is 0·8295 at 17·5°. It solidifies between + 5°—6° to a crystalline mass, which melts again at + 15°—16°. It boils constantly at 224°.

Commercial oil of rue was found to contain a considerable quantity of oil of turpentine; the portion boiling between 200°—245° consists chiefly of *nonyl-methyl ketone*, which was obtained perfectly pure by

* Ann. Ch. Pharm., clvii, 275—281.

proceeding as described above. The pure compound boiled at 224°—225°, and melted and solidified at the same temperatures as that obtained by synthesis. Its specific gravity is 0·8281 at 18·7°.

It is thus seen that oil of rue contains a large quantity of nonylmethyl ketone, which has also been proved lately by Giesecke and Fittig, who found that the purified oil of rue gives by oxidation *pelargonic* and *acetic* acid, in accordance with the law discovered by Popoff, who found that on oxidizing ketones, two acids are formed, one containing the same number of carbon-atoms as the higher alcohol-radical, whilst the lower radical remains combined with the group CO, forming thus the radical of the second acid.

C. S.

On the Circular Polarization of Castor Oil. By O. Popp.*

Castor oil possesses the property of rotating a ray of polarized light; the amount of rotation was observed of solutions of castor oil in absolute alcohol. 10 per cent. solutions of pure Italian and Ostend castor oils gave as a mean result, a direct deviation of 10° to the right, which gives as the specific rotating power of castor oil (α) = + 12·15°. This behaviour of castor oil, may be used as a test of its purity, although the specific rotating power is too small to allow small quantities of adulteration to be detected. Castor oil also contains a constant quantity of nitrogen, which is possibly due to the presence of an alkaloid. Popp is inclined to believe, that not only the purging properties, but also its circular polarization, are due not to the oil itself, but to the presence of this alkaloid.

A. P.

On the Decomposition of Cyanogen by Hydrochloric Acid in Alcoholic Solution. By J. Volhard.†

Hydrochloric acid and aldehyde convert cyanogen, in presence of water, into oxamide, without undergoing any change themselves; hence it might be inferred that in presence of alcohol these reagents would convert cyanogen into diethyloxamide, but this is not the case.

When cyanogen is passed into a saturated solution of hydrochloric acid in absolute alcohol, heat is evolved, and a white crystalline precipitate forms, in quantity proportionate to the cyanogen employed. Under these conditions, the precipitate is pure ammonium chloride; but if the solution be not saturated with hydrochloric acid, more or less oxamide is also produced; the mother-liquor contains no oxalic acid, but a small quantity of oxalic ether. A small quantity of formic ether

* Arch. Pharm. [2], cxlv, 233.

† Ann. Ch. Pharm., clviii, 118.

was discovered by pouring the mother-liquor of the crystalline precipitate into dilute aqueous solution of ammonia; separating the oxamide, acidifying the filtrate with sulphuric acid; distilling; saturating the distillate with calcium chloride; saponifying the ether which separates; and finally, distilling with dilute sulphuric acid. The distillate was acid, and gave the reactions of formic acid. No ethyl oxide seems to be present.

The decomposition occurs in the following manner:—

$$C_2N_2 + 4C_2H_5OH + 4HCl = C_2O_2(C_2H_5O)_2 + 2NH_4Cl + 2C_2H_5Cl.$$

F. H. H.

On some Double Cyanides. By P. Weselsky.*

The author prepares the double cyanides, the platinum compounds, for example, by passing a stream of hydrocyanic acid through a mixture of two equiv. barium carbonate and one equiv. platinous or platinic chloride: $PtCl_2 + 2BaCO_3 + 4HCN = Ba(CN)_2.Pt.(CN)_2 + BaCl_2 + 2CO_2 + 2H_2O$; and $PtCl_4 + 3BaCO_3 + 4HCN = Ba(CN)_2, Pt(CN)_2 + 2BaCl_2 + 2H_2O + 3CO_2 + O$.

I. Cyanides having the formula $Ba(CN)_2.R_2(CN)_2$.

1. *Barium-silver cyanide*, $Ba(CN)_2.Ag_2(CN)_2 + H_2O$. This salt, prepared from barium carbonate and silver carbonate, forms warty crystalline masses, which lose their water at 100°. 2. *Barium-zinc cyanide*, $Ba(CN)_2.Zn(CN)_2 + 2H_2O$, obtained from barium carbonate and zinc sulphate, forms large colourless crystals easily decomposed by exposure to the air. 3. *Barium-palladium cyanide*, $Ba(CN)_2.Pd(CN)_2 + 4H_2O$. This salt, already described by Rossler,† is formed from barium carbonate and palladium cyanide. 4. *Barium-nickel cyanide*, $Ba(CN)_2.Ni(CN)_2 + 3H_2O$. This well-known salt was prepared by the above-described method from nickel sulphate. 5. *Barium-copper cyanide*, $Ba(CN)_2.Cu_2(CN)_2 + H_2O$, prepared as above, forms large colourless crystals, which are decomposed by exposure to the air. A salt crystallising in fine needles is obtained from the mother-liquors. 6. *Barium-cadmium cyanide*, $2Ba(CN)_2.3Cd(CN)_2 + 10H_2O$, obtained from cadmium sulphate, crystallises well, but is very readily decomposed.

II. Cobalticyanides.

1. *Barium cobalticyanide*, $Ba_3CO_2(CN)_{12} + 20H_2O$. This salt, first prepared by Zwenger,‡ is easily obtained from barium carbonate, cobalt sulphate, and hydrocyanic acid, in bright yellow crystals. The cobalt sulphate need not be free from nickel, as the corresponding

* Zeitschr. f. Chem. [2], vii, 61, from Wien. Akad. Ber., lx, 261.

† Zeit. f. Chemie, 1866, 283.

‡ Ann. Chem. Pharm., lxii, 169.

nickel salt is easily separated, owing to its being far less soluble. 2. *Sodium cobalticyanide*, $Na_6Co_2(CN)_{12} + 4H_2O$; and, 3. *Ammonium cobalticyanide*, $(NH_4)_6Co_2(CN)_{12}$, have been already described by Zwenger. The author obtained them by decomposing barium cobalticyanide with sodium and ammonium sulphates. He also prepared in a similar manner:—4. *Phenylammonium cobalticyanide*, $(C_6H_5NH_3)_6Co_2(CN)_{12}$. It forms crystals 3—4 inches long, of the colour of the cairngorm. 5. *Tolylammonium cobalticyanide*, $(C_7H_7NH_3)_6Co_2(CN)_{12} + 4H_2O$, forms colourless crystals. The author employed the ammonium and phenylammonium compounds for the determination of the equivalent of cobalt. The substance was ignited in a platinum boat, first in the air, then in oxygen, and finally in hydrogen, and the metallic cobalt weighed. This process gave 29·48 as the equivalent. Winkler* found 29·496; the author, by the employment of Winkler's method, 29·42. 6. *Strontium cobalticyanide*, $Sr_3Co_2(CN)_{12} + 20H_2O$, obtained by exactly precipitating the barium salt with sulphuric acid, and boiling with strontium carbonate, forms large, very soluble crystals.

III. The author has moreover prepared compounds of the following kind:—

1. *Sodium-ammonium cobalticyanide*, $(NH_4)_4Na_2Co_2(CN)_{12}$, obtained in fine crystals by mixing the sodium and ammonium cobalticyanides; they dissolve with difficulty. Potassium and ammonium cobalticyanides are isomorphous and crystallise out together in variable quantities. 2. *Calcium-ammonium cobalticyanide*, $Ca_2(NH_4)_2Co_2(CN)_{12} + 20H_2O$, crystallises on mixing solutions of calcium and ammonium cobalticyanides. 3. *Calcium-potassium cobalticyanide*, $Ca_2K_2Co_2(CN)_{12} + 18H_2O$, separates from a mixture of potassium and calcium cobalticyanides in very fine crystals. 4. *Strontium ammonium cobalticyanide*, $Sr_2(NH_4)_2Co_2(CN)_{12} + 20H_2O$, crystallises well. 5. *Strontium-potassium cobalticyanide* is $Sr_2K_2Co_2(CN)_{12} + 18H_2O$. 6. *Barium-ammonium cobalticyanide*, $Ba_2(NH_4)_2Co_2(CN)_{12} + 22H_2O$, forms fine crystals. 7. *Barium-potassium cobalticyanide*, $Ba_2K_2Co_2(CN)_{12} + 22H_2O$. 8. *Barium-lithium cobalticyanide*, $Ba_2Li_2Co_2(CN)_{12} + 30H_2O$, is a very soluble salt. 9. *Tolyl-phenyl-ammonium cobalticyanide*, $(C_7H_{10}N)_4(C_6H_8N)_2Co_2(CN)_{12} + 3H_2O$, forms large crystals.

IV.—1. *Barium cobalticyanide with barium hydrate*, $Ba_3Co_2(CN)_{12}, BaH_2O_2 + 17H_2O$, is obtained in large crystals by evaporating *in vacuo* solutions of barium cobalticyanide with excess of barium hydrate. They are easily decomposed by carbonic acid. 2. *Barium cobalticyanide with barium chloride*, $Ba_3Co_2(CN)_{12}.BaCl_2 + 16H_2O$. This difficultly soluble salt crystallises from a mixture of the solutions, in tables, and can be recrystallised. 3. *Phenylammonium cobalticyanide with phenylammonium hydrate*, $(C_6H_8N)_6Co_2(CN)_{12}.2(C_6H_8N,HO)$, obtained by

* Zeit. f. Analyt. Chem., 1867, 18.

saturating a warm solution of phenylammonium cobalticyanide with aniline; it crystallises in prisms, which readily decompose. This salt has an *acid* reaction.*

C. E. G.

On Isomeric Potassium Cyanate. By A. BANNOW.†

THE author has made some experiments on the action of potassium hydrate on paracyanogen, whereby he has obtained a salt having the composition of potassium cyanate, but differing from it in some minute particulars. The new salt crystallises in long needles. It is formed under a great variety of circumstances, and may be separated from the common cyanate by crystallisation. Only one satisfactory reaction was observed in which it differed from the common cyanate. When the solution of the salt was treated for a long time with alkali, then neutralised and treated with nitrate of silver, a white precipitate unaffected by light was obtained, having the composition C_2N_3Ag. The author gives the following equation as possibly expressing its mode of formation:—

$$3CNOH = H_2CO_3 + C_2N_3H.$$

He quotes a recent observation of Dr. Melms to the effect that heating cyanate of potassium with iodide of cyanogen, converts the whole of the cyanate into the new salt, the iodide of cyanogen remaining unaltered. The author is in a position to confirm this observation.

E. T. C.

On the Isomeric Modification of Potassium Sulphocyanate. By A. FLEISCHER.‡

THE above-mentioned body is produced by the action of an alcoholic solution of potash on persulphocyanic acid. It is obtained as a yellowish granular mass, from which the yellow colour can be removed by boiling with very strong alcohol. It is, however, difficult to obtain it perfectly pure in this way. It can be freed from adhering water by exposure over oil of vitriol. Numbers were obtained, by analysis, agreeing pretty well with the formula KCNS. The new body dissolves easily in water, is almost insoluble in strong alcohol, but soluble in very weak alcohol. By allowing the aqueous solution to stand for a

* Wien. Akad. Ber., 1869, lx, 261.

† Deut. Chem. Ges. Ber., iv, 253—255.

‡ Deut. Chem. Ges. Ber., iv, 190.

long time in vacuo over sulphuric acid, crystals were obtained which had the composition $2KCNS + H_2O$. The following reactions distinguish the isosulphocyanate from the ordinary sulphocyanate:—

	Sulphocyanate.	Isosulphocyanate.
Silver nitrate	White precipitate, soluble in ammonia	Light yellow precipitate, scarcely soluble in ammonia.
Basic acetate of lead	White voluminous precipitate	Yellow precipitate.
Copper sulphate....	Black pulverulent precipitate	Greenish yellow precipitate.
Cobalt sulphate	Rose-red coloration.....	Brownish green precipitate.
Nickel sulphate	Greenish coloration.....	Reddish precipitate.
Cadmium sulphate..	.....	White precipitate.
Zinc chloride	No reaction	Deep yellow, voluminous precipitate.
Mercuric chloride ..	.....	White voluminous precipitate.
Mercurous nitrate	Grey precipitate	Black precipitate.

Ferric chloride gives, with neutral solutions of the new body, a brown coloration, which disappears on adding excess of the iron solution; a yellow pulverulent body separates from the liquid on standing.

Potassium isosulphocyanate may be partially converted into sulphocyanate by repeated evaporation of its aqueous or weak alcoholic solution on the water-bath. By fusing the new body, it is completely converted into sulphocyanate.

A smell, similar to that of mustard-oil, is observed by allowing ethyl iodide to stand with potassium or silver isosulphocyanate. Pseudosulphocyanogen appears likewise to be attacked by alcoholic potash and by ammonia; the author is engaged with the study of the products of this action.

W. H. D.

On Isodicyanic Ethers, Compounds intermediate between Cyanic and Cyanuric Ethers. By A. W. Hofmann.*

The author had previously observed that a drop of triethylphosphine caused liquid phenyl cyanate to solidify into a crystalline mass, which he then regarded as phenyl cyanurate. The preparation of a large quantity of this beautiful crystalline compound gave him an opportunity of comparing it with the phenyl-isocyanurate obtained by the action of cyanogen chloride on phenol, and also with that found amongst the decomposition-products of triphenylmelamine. These three bodies are not identical, as their melting points prove, phenyl-

* Deut. Chem. Ges. Ber., iv, 246—251.

cyanurate melting at 260° C., phenylisocyanurate at 224° C., the body from phenylcyanate at 175° C.

In a previous communication the author had asserted his belief, though without bringing forward observations in support of it, that this new body is a dicyanate intermediate between the cyanate and cyanurate—

$$\left.\begin{matrix}CO\\C_6H_5\end{matrix}\right\}N \qquad \left.\begin{matrix}(CO)_2\\(C_6H_5)_2\end{matrix}\right\}H_2 \qquad \left.\begin{matrix}(CO)_3\\(C_6H_5)_3\end{matrix}\right\}N_3.$$

The new body is not volatile without alteration, therefore its vapour density could not be determined. On distillation the body is reconverted into liquid phenyl cyanate, but the distillate so obtained exhibits the very peculiar property of resolidifying during 24 hours' standing, and this so perfectly that not the slightest trace of the smell of the fluid body can be perceived. This phenomenon is attributed to the presence and action of small quantities of the original crystalline substance; and to substantiate this view it was attempted to polymerize some of the liquid cyanate which had remained unaltered for months, by the addition of some crystals of the solid body. The experiment was a partial failure, for though the addition of the crystals appeared to induce solidification, a portion of the fluid remained unaltered even after a week's contact.

The problem which the vapour-density failed to solve received a simple solution when the behaviour of the crystalline body to various solvents was investigated. In purifying the substance for analysis, it became obvious that though the substance is only slightly soluble in ether, even on prolonged boiling, no other solvent could be used in its purification, as all other solvents alter it. By cooling and evaporation of the ethereal solution, very thin beautiful iridescent plates of the pure substance are obtained. On attempting to dissolve it by boiling in alcohol, some portion remained undissolved for hours; suddenly, however, the liquid became clear, and on cooling deposited fine needles, which by one recrystallisation from boiling alcohol were obtained pure. They are difficultly soluble in ether, and insoluble in water. They differ from the original body in form, in solubility in alcohol, and in their lower melting point (98°). Their analysis indicated the formula $C_{16}H_{16}N_2O_3$, which would be produced by the union of two molecules of phenyl cyanate and one of ethylic alcohol. The assumption that the polymerized body is a dicyanate, and that the new compound results from one molecule of it uniting with one of ethylic alcohol is, therefore, an extremely probable one—

$$C_{14}H_{10}N_2O_2 + C_2H_6O = C_{16}H_{16}N_2O_3.$$

Both the dicyanate and the unpolymerized cyanate act similarly to-

wards alcohol, each forming an urethane by combining with one molecule of it. There can scarcely be a doubt as to the nature of the alcohol compound of the dicyanate. No matter how we consider the elements to be grouped in the polymerized cyanate, it is clear that the relationship between the alcohol compound and the original fluid body is the same as that subsisting between Liebig and Wöhler's allophanate of ethyl and cyanic acid—

$CHNO$	Cyanic acid.
$C_3H_7NO_2 = CHNO,C_2H_6O$	Urethane.
$C_2H_2N_2O_2 = 2CHNO$.....	Two molecules of cyanic acid, or one molecule of dicyanic acid.
$C_4H_8N_2O_3 = 2CHNO,C_2H_6O$....	Allophante of ethyl.
$C(C_6H_5)NO$.....	Phenylcyanate.
$C_3H_6(C_6H_5)NO_2 = C(C_6H_5)NO, C_2H_6O$	Phenylurethane.
$C_2(C_7H_5)_2N_2O_2 = 2\{C(C_6H_5)NO\}$	Phenyldicyanate.
$C_4H_6(C_6H_5)_2N_2O_3 = 2\{C(C_6H_5)NO\}C_2H_6O$	Diphenylallophanic ether.

By distillation of diphenylallophanic ether, alcohol and phenyldicyanate are regenerated, the latter being almost entirely converted into simple cyanate.

Diphenylallophanic methyl-ether, easily obtained pure by dissolving dicyanate in methylic alcohol and recrystallising from alcohol, forms difficultly-soluble needles, which melt at 231° C., or 133° higher than the corresponding ethyl compound.

Diphenylallophanic amyl-ether, obtained by dissolving the dicyanate in amylic alcohol, forms colourless and scentless crystals, insoluble in water, easily soluble in ether and alcohol, and melting at 58° C. This compound often remains long fluid.

Sulphuretted diphenylallophanic amyl-ether.—The dicyanate can unite with mercaptans as well as with alcohols; heated with amylic mercaptan for some hours at a temperature of 160° C., the dicyanate dissolves, and gradually the mixture solidifies to a white crystalline mass. Recrystallised from alcohol or ether, the new body forms colourless and scentless needles, which melt at 70° C. The body is insoluble in water. Analysis led to the formula—

$$C_{19}H_{22}N_2O_2S = 2\{C(C_6H_5)NO\},C_5H_{12}S.$$

Action of Phenol on Phenyldicyanate.—These two substances act upon each other at 150° C., but do not yield the phenyl ether as might have been expected. The experiment was conducted precisely as in the preparation of the former compounds. The dicyanate was digested with excess of phenol in ethereal solution; after some hours needles were produced, difficultly soluble in water, melting in contact with boiling

water, and easily soluble in alcohol. Melting point of the dry crystals 122° C. Analysis proved this body to be *phenylcarbaminic phenyl ether*, obviously produced by the splitting up of the dicyanate into the unpolymerized cyanate, which then united with the phenyl—

$$C_{14}H_{10}N_2O_2 + 2C_6H_6O = 2C_{13}H_{11}NO_2.$$
$$C_{13}H_{11}NO_2 = (CO)(C_6H_5)HN \left.\begin{matrix} \\ C_6H_5 \end{matrix}\right\} O.$$

On repeating the experiment with one atom of phenol to one of the dicyanate, the same result was obtained, half of the cyanate appearing as free phenyl cyanate; no phenylic ether of the dicyanate was obtained. The phenyl-carbamic phenyl-ether was prepared directly by the action of phenyl cyanate on phenylic alcohol; it agreed precisely with that obtained as above.

Just as a molecule of alcohol, by uniting with one or two atoms of cyanic acid, yields respectively urethane or allophanate of ethyl, so does ammonia yield urea or biuret. If the polymerizing of the cyanate consists in the union of two cyanate molecules, the resulting dicyanate must by union with different ammonias give rise to an endless series of biurets. This proves to be really the case.

Diphenylbiuret is formed instantly by pouring an alcoholic solution of ammonia over finely powdered dicyanate. The new body is insoluble in water, difficultly soluble in ether, but more easily soluble in alcohol. The boiling saturated alcoholic solution deposits well formed prisms with truncated pyramidal summits, melting at 165° C. Analysis proved these crystals to have the composition of diphenylbiuret—

$$C_{14}H_{13}N_3O_2 = C_2(C_6H_5)_2H_3N_3O_2.$$

If a monamine be substituted for the ammonia, a more complicated biuret will result.

Triphenylbiuret is produced by long digestion of one molecule of dicyanate and one molecule of aniline on the water-bath, when the two substances unite to a crystalline mass; by recrystallisation from alcohol prisms with true terminal planes are obtained. This body closely resembles diphenyl-urea, but melts at 147° C., instead of 235° C. Its formula is $C_2(C_6H_5)_3H_2N_3O_2$.

The composition of this triphenylbiuret was studied with great care, as Schiff has described a body of the same composition obtained in a somewhat complicated reaction. The two bodies have however nothing in common except their composition. If diphenylcyanate be heated to the boiling point with excess of aniline, the diphenylurea is produced.

$$C_{14}H_{10}N_2O_2 + 2C_6H_7N = 2C_{13}H_{12}N_2O = 2\{C(C_6H_5)_2H_2N_2O\}.$$

E. T. C.

On Biuret and Compounds allied to it. By A. W. HOFMANN.*

UREA is so easily transformed into biuret, that this reaction may be used as a test for urea or as a lecture experiment. It is only necessary to heat half a gramme or even less of urea until ammonia escapes, to obtain a considerable quantity of biuret, the presence of which is shown by dissolving the residue in water and adding a few drops of a solution of copper sulphate and an excess of soda. If very little copper sulphate has been taken, the liquid assumes a pale red colour, but if an excess has been used, a deep violet colour appears.

To prepare large quantities of biuret, the author heated urea according to Wiedemann's direction, in an oil bath to 150°—160°; as soon as the residue no longer dissolves completely in water, the reaction is finished. The product is now boiled out with water and the biuret, which separates out on cooling, is obtained in a perfectly pure state by recrystallising it first repeatedly from water and at last from dilute ammonia. From the insoluble residue a large quantity of cyanuric acid may be obtained; the mother-liquors of the biuret contain undecomposed urea, which may be employed in a second operation.

Biuret is not *readily* soluble in cold water, as Wiedemann states; 100 parts require at 0°, 8025 parts; at 15°, 6493 parts; and at 106° (the boiling point of the concentrated solution) 222 parts of water. Wiedemann obtained it only in granular crystals; but if biuret is completely freed from cyanuric acid by crystallising it from alcohol, it crystallises in fine long needles, and is identical and not isomeric with the body which Baeyer obtained by the action of ammonia upon tribromacetyl urea, and which he called *isobiuret.*

Biuret is also formed by heating ethylic allophanate with aqueous ammonia in sealed tubes to 100°:

$$C_2H_2N_2O_2,C_2H_6O + H_3N = C_2H_2N_2O_2,H_3N + C_2H_6O.$$

The melting point of biuret is stated differently by different authors; the reason of this is, that this point is the temperature of decomposition, which may vary according to the quantities taken or the mode of heating.

Ethylamine does not act upon ethylic allophanate; if the two substances are heated together in sealed tubes to 160°, the same decomposition takes place, which water alone produces, urethan, carbonic dioxide, and ammonia being formed.

When allophanic ether is heated with aniline to the boiling point, *α-diphenylbiuret* is obtained, which is sparingly soluble in alcohol, from which it crystallises in densely interwoven needles, which melt at 210°. This compound is formed according to the equations—

* Deut. Chem. Ges. Ber., iv, 262—268.

$$(1)\ C_2H_2N_2O_2.C_2H_6O + (C_6H_5)H_2N = C_2H_2N_2O_2.(C_6H_5)H_2N + C_6H_6O.$$

$$(2)\ C_2H_2N_2O_2.(C_6H_5)H_2N + (C_6H_5)H_2N = C_2H(C_6H_5)N_2O_2(C_6H_5)H_2N + H_3N.$$

The same body is formed directly when aniline is boiled for some time with biuret—

$$C_2H_2N_2O_2.H_3N + 2(C_6H_5)H_2N = C_2H(C_6H_5)N_2O_2.(C_6H_5)H_2N + 2H_3N.$$

α-diphenylbiuret is isomeric with β *diphenylbiuret*, which the author has obtained from phenylic dicyanate (*Deut. Chem. Ges. Ber.* iv, 246); the β-compound is readily soluble in alcohol, and melts at 165°.

When dry hydrochloric acid is passed over the α-compound, phenylic cyanate and aniline are formed, the cyanic acid which is set free, escapes, probably in combination with hydrochloric acid. The β compounds yield under the same circumstances the phenylic cyanate and ammonia; the two isomerides have therefore the following structure:—

α-Phenylbiuret..	C	H	NO.	$C(C_6H_5)NO$.	$(C_6H_5)H_2N$.
β-Phenylbiuret..	$C(C_6H_5)NO$.			$C(C_6H_5)NO$.	H_3N.

As in the preparation of biuret a large quantity of urea is always left undecomposed, and another portion is converted into cyanuric acid, Baeyer has proposed to heat urea in presence of phenol, in order to avoid overheating; but in this case also a considerable quantity of cyanuric acid is always formed. The author therefore tried amyl alcohol, which boils at a lower temperature, but instead of biuret, he obtained *amylic allophanate*, $2CHNO.C_5H_{12}O$, besides *amylic urethane*, $CHNO.C_5H_{12}O$. The allophanate is completely converted into the urethane, if it is heated with amyl alcohol in sealed tubes, to 160°—180°.

When urea and ethylic alcohol were boiled together for 36 hours, only ethylic urethane was formed.

It is thus seen that whenever cyanic acid or a cyanate is acted upon by an alcohol in excess, an urethane is formed; but if the cyanate preponderates, an allophanate is obtained.

C. S.

On a Homologue of Cyanethine. By A. G. Bayer.*

This communication is an addition to the history of cyanmethine, a base already described by the author.

Chlorine gas readily acts on cyanmethine in aqueous solution, form-

* Deut. Chem. Ges. Ber., iv, 176.

ing chlorocyanmethine and hydrochloric acid. To prevent the action of the chlorine going too far, it is well to guard against rise of temperature. The chlorocyanmethine is obtained by crystallisation from hot water in long, four-sided needles, which contain 3 molecules of water. By exposure to air or to a temperature of 100°, the water is expelled, leaving the anhydrous base, $C_6H_8ClN_3$. The chlorine is held very firmly by this body; attempts to substitute it by the action of potassium hydrate, iodide, and silver oxide, gave no satisfactory result. Treatment with sodium amalgam, however, converts the chloro-derivative into cyanmethine.

The further action of chlorine on chloro-cyanmethine does not produce the dichlor-amine, but hydrochloric acid, ammonia, acetic and chloracetic acids.

Bromine acts upon cyanmethine, forming the body $C_6H_8BrN_3 + 3H_2O$, the properties of which are very similar to those of the corresponding chlorine derivative.

Cyanmethine unites with iodine to form numerous periodides; for instance, by adding tincture of iodine by small portions to an aqueous solution of the base, crystals are obtained, having the composition $C_6H_9N_3.I_2$ Light reflected from the crystals appears red; but when transmitted through them, yellow. By boiling with water the diniodide loses all its iodine, and almost the whole of the cyanmethine is found in the liquid. Hydriodate of cyanmethine can likewise unite with two atoms of iodine, forming the compound $C_6H_9N_3,HI_3$, which also loses iodine by boiling with water, reproducing hydriodate of cyanmethine. By repeating on the body $C_6H_9N_3,HI_3$ the treatment with tincture of iodine, a pentaiodide, $C_6H_9N_3,HI_5$, is obtained. It occurs in dark blue prisms, and is very prone to decomposition. Bayer considers that the existence of these compounds supports the views which would make the atomic weight of iodine = 381; he gives representations of their structure, in which the iodine has that value assigned to it.

W. H. D.

On the Periodides of the Alkaloïds. By S. M. Jörgensen.*

Periodides of the Quinine Bases.—The tri-iodide of methylquinine, $C_{20}H_{24}N_2O_2.CH_3,I_3$, is obtained by adding a solution of 2 atoms of iodine in alcohol to a hot alcoholic solution of the hydriodate of methyl-quinine. By slow cooling of the liquid the tri-iodide is formed in beautiful black needles, with diamond-like lustre. This body is pretty readily soluble in alcohol; the brown solution is decolorised by sulphurous acid, sulphuretted hydrogen, or by mercury. The tri-iodide, by boiling with a large quantity of water, gradually loses the 2 atoms

* J. pr. Chem. [2], iii, 145—176.

iodine, and is reduced to the state of hydriodate of methylquinine. It does not appear to be decomposed by boiling with strong ammonia solution, or by cold solution of sodium hydrate; it is, however, easily and completely decomposed by solution of silver nitrate.

The method of preparation adopted for the above compound is that employed, with scarcely an exception, in the formation of tri-iodides of numerous other bases. Their properties, including angular measurements, are given in great detail; but what has been said of the methylquinine derivative may be taken as a type of the whole.

Of the quinine-bases, the following iodides have been obtained:—

Tri-iodide of	Ethylquinine	$C_{20}H_{24}N_2O_2.C_2H_5.I_3$
,,	Cinchonine.....	$C_{20}H_{24}N_2O.H.I_3 + H_2O$.
,,	Methylcinchonine..	$C_{20}H_{24}N_2O.CH_3.I_3$
,,	Ethylcinchonine ..	$C_{20}H_{24}N_2O.C_2H_5.I_3$.
,,	Methylquinidine ..	$C_{20}H_{24}N_2O_2.CH_3.I_3$.
,,	Methylcinchonidine	No analytical numbers given.

In connection with the tri-iodide of cinchonine, $C_{20}H_{24}N_2O.H.I_3 + H_2O$, an interesting experiment was made, which shows that 2 atoms of the iodine are held very loosely. An alcoholic solution of the tri-iodide was decolorised by a standard solution of sodium hyposulphite. For complete decolorisation, sodium hyposulphite was consumed equivalent to 36·0 per cent. I; calculated percentage for 2 at. I = 35·88.

Periodides of the Strychnine Bases.—The method of preparation, and description of these compounds, have been already given by Jörgensen. The tri-iodides of simple or substituted strychnine or brucine, seem to have great similarity to the corresponding quinine derivatives. They are dark-coloured, well crystallised bodies; their alcoholic solution is decolorised by reducing agents. On heating them with a large quantity of water, 2 at. I are given off, and the hydriodate of the base is produced. The following have been obtained:—

Tri-iodide of	Strychnine	$C_{21}H_{22}N_2O_2.HI_3$.
,,	Methylstrychnine	$C_{21}H_{22}N_2O_2.CH_3.I_3$.
,,	Bromethylene-strychnine	$C_{21}H_{22}N_2O_2.C_2H_4Br.I_3$.
,,	Amylstrychnine	$C_{21}H_{22}N_2O_2.C_5H_{11}.I_3$.
,,	Brucine	$C_{23}H_{26}N_2O_4.HI_3$.
,,	Methylbrucine	$C_{23}H_{26}N_2O_4.CH_3.I_3$.
,,	Ethylbrucine	$C_{23}H_{26}N_2O_4.C_2H_5.I_3$.
,,	Amylbrucine	$C_{23}H_{26}N_2O_4.C_5H_{11}.I_3$.
,,	Allylbrucine	$C_{23}H_{26}N_2O_4.C_3H_5.I_3$.

A class of pentiodides has also been obtained, containing the following members:—

Pentiodide of Methylbrucine ..	$C_{23}H_{26}N_2O_4.CH_3.I_5$.
,, Ethylbrucine	$C_{23}H_{26}N_2O_4.C_2H_5.I_5$.
,, Allylbrucine	$C_{23}H_{26}N_2O_4.C_3H_5.I_5 + H_2O$.

The mode of preparing these compounds is not given in the present paper; they form crystals having an almost metallic lustre, and behave towards reagents very much like the tri-iodides.

It is remarked of the pentiodide of ethylbrucine that, in crystallising it from hot alcohol, a small quantity of iodine is lost by each crystallisation. After 8—10 crystallisations, the tri-iodide comes down with the pentiodide. Crystallisation of the pentiodide from a strong solution of iodine causes it to take up an excess of iodine. By adding potassium iodide to a solution of brucine in hydrochloric acid, and leaving the mixture to slow oxidation, reddish-yellow needles were obtained, having the composition of a di-iodide of brucine, $C_{23}H_{26}N_2O_4HI_2$. This compound is probably a double salt of hydriodate and tri-iodide of brucine. At least, on cooling an alcoholic solution of this compound, crystals of the tri-iodide were deposited, and the filtrate from these crystals contains hydriodate of brucine.

A substance having the composition of a hexiodide of amylbrucine, $C_{23}H_{26}N_2O_4.C_5H_{11}.I_6$, was obtained by adding to an alcoholic solution of the tri-iodide the calculated quantity of iodine. It appears in the form of bluish-green needles. The hexiodide is difficultly soluble, even in boiling alcohol; from this solution the tri-iodide separates out on cooling.

Igasurine.—Jörgensen, in the hope of settling the question whether this alkaloid exists or not, endeavoured to prepare a periodide from it. A preparation by Menier, called igasurine, was dissolved in dilute hydrochloric acid, and fractionally precipitated by a solution of iodine in potassium iodide. The two precipitates thus obtained were washed with cold water and crystallised from alcohol. In both cases violet-brown crystals were obtained, which had the optical properties and crystalline form of tri-iodide of brucine. (I) contained 49·1 per cent. I; (II) 49·05 per cent. I; tri-iodide of brucine contains 49·10 per cent. I.

W. H. D.

On the Synthesis of Conine. By Hugo Schiff.*

The author's researches on the formation of oxyaldine by the action of ammonia on aldehyde,† and the products of its decomposition, led him to the conclusion that conine and chinoline (probably also nicotine and piperidine) belong to the same class of substances: an inference

* Ann. Chem. Pharm., clvii, 352—362.

† *Ibid.*, Suppl., vi, 1.

strengthened, in the case of conine, by the existence of butyric acid among the oxidation-products of this base.

In order to test this conclusion, normal butyric aldehyde obtained by heating calcium butyrate with calcium formate was converted into more condensed products by heating to 70°—90° with concentrated hydrochloric acid solution in sealed tubes; and a fraction of the product passing over below 250° was heated with alcoholic solution of ammonia to 100°, and for a shorter time to 140°—150°. The thick oil so obtained smelt somewhat like conine, but consisted chiefly of resinous substances, affording no satisfactory results.

Butyric aldehyde was then treated for two months with alcoholic solution of ammonia at about 30°, and for one day at 100°. Experiments proved that the product might be at once gently heated on the water-bath, neutralized with hydrochloric acid, and fractionally precipitated with platinic chloride. In this manner, a yellow flocculent precipitate answering to $2C_{16}H_{29}NO.H_2PtCl_6$ forming the greater part of the product of the reaction, was obtained. The base contained in this salt corresponds to a condensation of 4 molecules of butyric aldehyde—

$$\underset{\text{Tetrabutyraldine.}}{C_{16}H_{29}NO} = 4C_4H_8O + NH_3 - 3H_2O.$$

Neither the base nor its hydrochloride is crystallisable. The mother-liquor from this compound gave by further treatment a yellow crystalline powder $2C_8H_{17}NO.H_2PtCl_6$, the base of which represents the condensation of two molecules of butyric aldehyde—

$$\underset{\text{Dibutyraldine.}}{C_8H_{17}NO} = 2C_4H_8O + NH_3 - H_2O.$$

This substance exists in a small proportion only in the crude product.

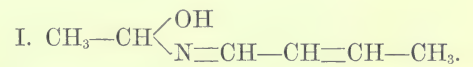
The dibutyraldine platinochloride was then decomposed by sulphydric acid and treated with concentrated solution of potash. On distilling the free base with quartz-sand in an oil-bath, water, ammonia, and oily products passed over. The distillate was freed from ammonia by gentle heating, neutralised with hydrochloric acid to separate tarry substances, concentrated, and precipitated with platinic chloride. By recrystallisation from alcohol the precipitate was obtained as an orange-coloured crystalline powder, consisting of conine platinochloride $2(C_8H_{15}N).H_2PtCl_6$. The mother-liquor gave an obscurely crystalline substance yielding only 20 per cent. platinum, probably a more highly condensed base produced by decomposition of the dibutyraldine.

The free conine base was separated from the platinum salt by potash and ether, and presented itself of an amber colour, becoming quickly

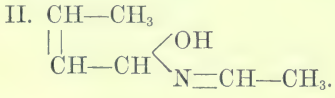
darker coloured and less fluid in the air. In its chemical reactions it closely resembled natural conine, with the following differences: A minute quantity of the base gave with auric chloride a yellow precipitate which turned violet much more slowly than the analogous precipitate obtained with the natural base. This is a novel reaction of conine, and does not ensue with chinoline, amylamine, or trimethylamine. Artificial conine gives with concentrated hydrochloric acid a greenish-blue colour; the natural base gives a pure indigo-blue. The natural base precipitates argentic hydrate immediately at the ordinary temperature, the artificial requires more time and gentle warmth (about 40°). The platinochloride of the artificial is less soluble in water than that of the natural base. The physiological properties of the artificial base coincide with those of natural conine.

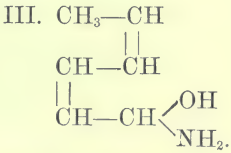
The author intends to examine the products to be obtained by means of the aldehyde derived from fermentation butyl alcohol, and also to see whether dibutyraldine is identical or isomeric with Wertheim's conydrine.

The combination, under the influence of ammonia, of several aldehyde residues may occur in two essentially different ways, accordingly as the nitrogen or the carbon forms the uniting link in the chain; and the author has shown that aldehydes easily act upon primary and secondary amines, substituting aldehyde-residues for typical hydrogen (in union with nitrogen), water being eliminated. The recently-discovered constitution of crotonic aldehyde permits the constitution of oxytrialdine (*loc. cit.* p. 5) to be exhibited by the formula—

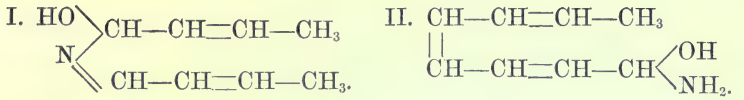


whence it would be isomeric with the product of the action of acetic aldehyde on aldehyde ammonia, and with the ammonia derivative of a thrice-condensed acetic aldehyde.

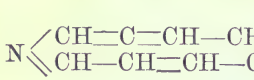




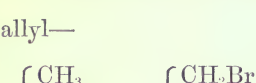
The removal of water from oxyaldine (*loc. cit.* p. 20) gives rise to bases belonging to the pyridine series in which Anderson and Baeyer's researches indicate the existence of isomerides. The three formulæ above given lead to four isomerides, C^6H^9N; the platinochloride of one of these was described by the author (*loc. cit.* p. 22). Similarly two formulæ arise for oxytetraldine (*loc. cit.* p. 10).



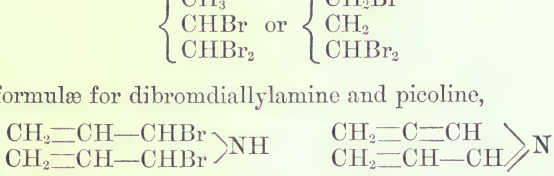
As Baeyer and Ador's colidine (*Ann. Ch. Pharm.* clv, 294) contains no typical amidic hydrogen, it is probably derived from formula I, being—



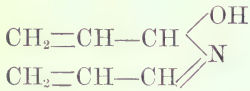
So also from tribromallyl—



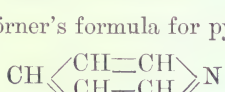
arise the formulæ for dibromdiallylamine and picoline,



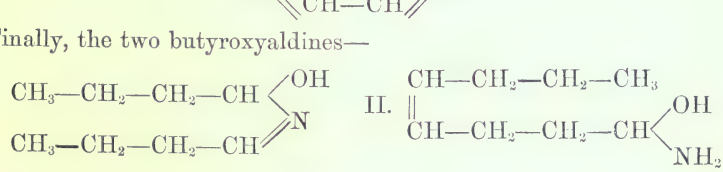
the latter being also derivable from acrolein-ammonia,



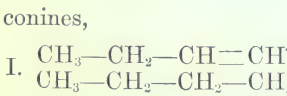
and closely related to Körner's formula for pyridine.

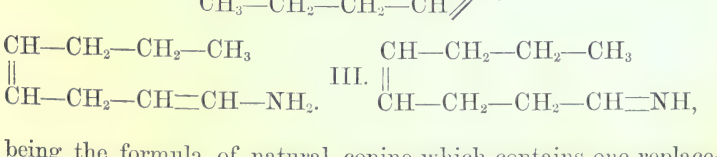


Finally, the two butyroxyaldines—



give three isomeric conines,





III. being the formula of natural conine which contains one replaceable hydrogen-atom, and in which Wertheim has proved the bivalence of the group C^8H^{14} (conylene).

Other isomerides of butyryl-conine may perhaps be made from isobutyric aldehyde or a mixture of this with normal butyric aldehyde.

A great number of other isomerides may perhaps arise from the

combination, under the influence of ammonia, of the residues of acetic or propionic aldehydes with those of normal or abnormal caproic and valeric aldehydes.

F. H. H.

On the action of Hydrobromic Acid on Codeine. By C. R. A. WRIGHT.*

MATTHIESSEN showed† that when codeine is heated with a large excess of strong hydrochloric acid, the following reactions successively take place:—

$$\underset{\text{Codeine.}}{C_{18}H_{21}NO_3} + HCl = H_2O + \underset{\text{Chlorocodide.}}{C_{18}H_{20}ClNO_2}.$$

$$\underset{\text{Chlorocodide.}}{C_{18}H_{20}ClNO_2} = CH_3Cl + \underset{\text{Apomorphine.}}{C_{17}H_{17}NO_2}.$$

When codeine is gently heated with hydrobromic acid, the first stage of the reaction appears to be similar to that of hydrochloric acid, yielding bromocodide, $C_{18}H_{20}BrNO_2$, analogous to chlorocodide; but this base appears to be further acted on with great ease, giving rise to two others, viz., deoxycodeine, $C_{18}H_{21}NO_2$, soluble in ether, and bromotetracodeine, $C_{72}H_{83}BrN_4O_{12}$, insoluble in ether. These reactions may be represented as follows:—

$$\underset{\text{Bromocodide.}}{C_{18}H_{20}BrNO_2} + \underset{\text{Codeine.}}{4C_{18}H_{21}NO_3} = \underset{\text{Deoxycodeine.}}{C_{18}H_{21}NO_2} + \underset{\text{Bromotetracodeine.}}{C_{72}H_{83}BrN_4O_{12}}.$$

Bromocodide is not easily obtained pure on account of the facility with which it is altered; but by digesting 1 part of codeine at 100° for an hour or two with 3 parts of acid solution (containing 48 p. c. HBr); precipitating with excess of sodium carbonate; filtering to remove excess of codeine, which remains dissolved; exhausting the precipitate with ether; and agitating the ethereal solution with hydrobromic acid, crude hydrobromide of bromocodide is obtained; and by repeating the process and precipitating fractionally to remove colouring matters, the purified hydrobromide is obtained, yielding by analysis numbers agreeing nearly with the formula $C_{18}H_{20}BrNO_2.HBr$.

Crude bromocodide hydrobromide, obtained by digesting codeine for five or six hours with from three to five times its weight of acid containing 48 per cent. HBr, deposits, on standing for some days, crystals not readily soluble in cold water; these recrystallised several times from boiling water, produce minute snow-white crystals which slightly darken in colour on drying over oil of vitriol, and on analysis give

* Proc. Roy. Soc., xix, 371.

† Ibid., xvii, 460; xviii, 83.

numbers agreeing with the formula of deoxycodeine hydrobromide, $C_{18}H_{21}NO_2.HBr$.

Bromotetracodeine is conveniently obtained as hydrobromide by treating codeine with three times its weight of hydrobromic acid containing 48 p. c. HBr for two hours on the water-bath, precipitating the product (diluted with water) with excess of sodium carbonate, exhausting the well-drained precipitate with ether, dissolving the residue in the smallest possible quantity of weak hydrobromic acid, and fractionally precipitating by cautious addition of stronger acid. The second precipitate is dissolved in water, in which it is readily soluble, and a few drops of solution of sodium carbonate are added. The filtrate from this yields, with strong hydrobromic acid, nearly white flakes, which are wholly devoid of crystalline character under the microscope. These remain solid at 100°, if previously completely dried over oil of vitriol, but, if warmed while moist, become a more or less coloured tar. Dried at 100°, they give numbers agreeing with the formula, $C_{72}H_{83}BrN_4O_{12}.4HBr$.

Sodium carbonate throws down from the hydrobromide a nearly white precipitate, which rapidly darkens, and finally becomes deep green or nearly black, owing to rapid absorption of oxygen; an analysis of the altered product gave the formula for bromotetracodeine plus 9 atoms of oxygen; the salts, however, when dry, may be kept without alteration, and only slowly darken by exposure to air when moist.

The qualitative reactions of bromotetracodeine appear to be identical with those of bromo- and chlorocodide. The base itself, when freshly precipitated, is slowly soluble in water, being thrown down again by the addition of strong brine; in ether and benzol it is almost insoluble, and in alcohol but sparingly soluble.

When crude bromotetracodeine is dissolved in weak hydrochloric acid, and precipitated twice or thrice by excess of stronger acid, nearly white flakes are ultimately obtained, which, dried over oil of vitriol and finally at 100°, have the composition of the hydrochloride of chlorotetracodeine, $C_{72}H_{83}ClN_4O_{12}.4HCl$.

Chlorotetracodeine, in all its physical and chemical properties, closely resembles bromotetracodeine; their qualitative reactions are identical, they have an intensely bitter taste, and apparently but slight physiological action, at any rate in small doses.

J. B.

On Hyoscyamine. By Ernst Thorey.*

After a careful examination of the methods already published for the extraction of hyoscyamine, the author gives the preference to the

* Zeitschr. f. Chem. [2], vii, 58, from Pharm. J. für Russland, 1869, p. 265.

following:—The crushed henbane seeds are digested two or three times with petroleum oil at 30°—40°; the resulting greyish-white powder is digested for 48 hours at 30° with 85 per cent. alcohol, to which a few drops of hydrochloric acid have been added; the alcoholic solution is pressed out, and the greater portion of the alcohol distilled off. Water is now added to complete the separation of the resin, and the solution concentrated by evaporation, first on a water-bath, and finally in vacuo. The small quantity of acid liquid thus obtained is agitated with chloroform to remove traces of resin, separated from it, and then rendered alkaline by potash. The alkaloïd is now taken up by agitating the solution with successive quantities of chloroform, washing the chloroform solution with pure water, and finally extracting it with very dilute acid, when it is obtained by evaporation and washing with absolute alcohol as a yellowish-white salt.

The sulphate crystallises in long glistening needles. The pure hydrochloride is a white mass, with bitter taste, and alkaline reaction. It crystallises from chloroform in rhombic tables, and from benzol in fine needles. It is soluble in warm water, dilute alcohol, ether, chloroform, benzol, amyl alcohol, and dilute acids, slightly soluble in water at the ordinary temperature, and in absolute alcohol. Its solutions in hydrochloric, sulphuric, nitric, phosphoric, and acetic acids yield crystalline compounds.

Solutions of hyoscyamine give with potassium-bismuth iodide a red amorphous precipitate; with sodium phosphomolybdate, yellow, becoming blue on standing; with gold chloride, yellow crystalline; with aqueous solution of iodine, dark orange red; with tannin, an amorphous yellowish-grey precipitate. Picric acid precipitates hyoscyamine yellow. Caustic potash and its carbonate, as well as ammonia, precipitate it incompletely, especially the latter. All parts of the plant contain the alkaloïd, the dried leaves the most, then the fruit; the root and the stems least. The author says that, besides "hyoscyamine and nitre," the plant also contains a resin and an acid.

C. E. G.

On Hofmann's Tyrosine Reaction, and on the Compounds of Tyrosine and Mercury. By M. von. Vintschgau.*

The author has observed that, when dilute mercury nitrate is added to a very dilute boiling solution of tyrosine until a precipitate begins to be formed, and the solution is set aside to cool, four-sided microscopic prisms or needles are deposited, which are but little soluble in water. Dried at 100°, they have the composition $C_9H_{11}NO_3.2HgO + 2H_2O$. If a solution of mercury nitrate be added to the boiling tyrosine solution

* Zeitschr. f. Chem [2], vii, 62, from Wien. Akad. Ber., lx, 276.

as long as a precipitate is produced, a yellow amorphous substance, $C_9H_{11}NO_3.3HgO + 2H_2O$, is obtained. C. E. G.

The Acetyl Derivatives of Ammonia. By H. WICHELHAUS.*

TRIACETAMIDE can be prepared by heating together acetonitrile and acetic anhydride; but the yield is small, even when the mixture is exposed for several hours to a temperature of 200°. When the excess of acetic anhydride has been removed by distillation, the residue is purified by crystallisation from dry ether.

The appearance and properties of the small white flexible needles thus obtained, were so similar to those of diacetamide, and moreover the melting points of the two were so close to one another, that it was necessary to confirm the formula $(C_2H_3O)_3N$ by analysis. The compound, when pure, melts at 78° to 79°, and again solidifies at a somewhat lower temperature. Diacetamide melts at 74° to 75°, and acetamide, as is well known, at 78°; the melting points of all three are therefore very near one another. They are also likely to be mistaken in other respects, as diacetamide, like acetamid, when treated with silver oxide in the cold, dissolves, with formation of a peculiar salt, whereas triacetamide at first forms no such compound. Yet when gently warmed, all three form acetates. Acetamide, however, retains its well-known odour when dissolved; diacetamide under the same circumstances gives an acid reaction, and triacetamide is neutral. Diacetamide, when treated with phosphoric anhydride, yields acetonitrile and acetic acid or its anhydride. C. E. G.

On the direct Substitution of the Alcohol-radicals for the Hydrogen in Phosphoretted Hydrogen. By A. W. HOFMANN.†

IODIDE of phosphonium was placed in a tube with an inner open tube containing ethylic iodide and water; after sealing up, it was exposed to a temperature of 160°—180° for 10 hours. On opening, large quantities of phosphoretted hydrogen and hydriodic acid were evolved, and the tube was found to contain small quantities of phosphorus bases. Iodide of phosphonium was then heated with absolute alcohol to the same temperature, and on cooling, the tube was found to contain a beautiful snow-white crystalline mass, from which were obtained almost equal parts of triethylphosphine and tetrethylphosphonium iodide; the reactions proceed according to the following equations:—

$$H_3P.HI + 3(C_2H_5.HO) = (C_2H_5)_3P.HI + 3H_2O.$$
$$H_3P.HI + 4(C_2H_5.HO) = (C_2H_5)_4P.I \quad + 4H_2O.$$

* Zeitschr. f. Chem. [2], vii, 45, from Deut. Chem. Ges. Ber., iii, 847.

† Deut. Chem. Ges. Ber., iv, 205.

The reactions really take place in two stages, for ethylic iodide and phosphoretted hydrogen are first formed; this was proved by exposing a tube for only four hours to 180°. On opening, streams of gas were evolved, and ethylic iodide was found in the tube. Iodide of phosphonium and methylic alcohol react on each other in a perfectly similar manner, producing trimethylphosphonium iodide and tetramethylphosphonium iodide.

The perfect analogy of these to the ammonia reactions makes it possible, that mono- and di-ethylated phosphoretted hydrogen may be obtained, under fit conditions, by this method.

This reaction, too, will enable us to obtain the phosphorus bases with the whole series of alcohols, and in fact to form all the bodies corresponding to the compound ammonias. Experiments are already being tried on various bodies.

A. P.

On a New Constituent of White Mustard Seed. By H. WILL.*

WHITE mustard seed contains a glucoside, sinalbin, which is soluble in alcohol, and like potassium myronate decomposes in contact with aqueous extract of mustard:—

$$\underset{\text{Sinalbin.}}{C_{30}H_{44}N_2S_2O_{16}} = \underset{\substack{\text{Acrinyl}\\\text{Sulphocyanate.}}}{C_8H_7NSO} + \underset{\substack{\text{Sinapirine}\\\text{sulphate.}}}{C_{16}H_{19}NSO_9} + \underset{\text{Sugar.}}{C_6H_{12}O_6},$$

an albuminous substance being likewise formed. Acrinyl sulphocyanate resembles oil of mustard, is soluble in ether, very pungent, insoluble in water, but not volatile; after warming with an alkali and neutralisation with an acid, it gives a red colour with ferric chloride. Sinapirin sulphate is insoluble in ether.

Sinalbin gives a white precipitate with silver nitrate, from which sulphydric acid removes the silver, leaving acrinyl cyanate, C_8H_7NO, fusible at 69°, easily soluble in water, alcohol, and ether. When boiled with potash, it gives ammonia and the potassium salt of an acid, $C_8H_8O_3$, fusible at 136°, but apparently different from the known acid of this composition.

The author does not describe the relations borne by these compounds to those constituents of mustard which are already known.

F. H. H.

* Zeitschr. f. Chem. [2], vii, 89, from Wien. Akad. Ber., lxi, 178.

A neutral, crystallisable Principle in Black Snake-root (Cimicifuga racemosa). By T. Ellwood Conard.*

The active principle of *Cimicifuga racemosa* appears to be a neutral, crystallisable body. The fresh root bruised and treated with alcohol produces a tincture, which, after the separation of the resin, tannin, &c., by acetate of lead, leaves, on spontaneous evaporation, a powder which may be purified from fatty matter by benzol. The powder freed from the odour of benzene, washed with water, dried, dissolved in alcohol, mixed with pure alumina, and evaporated spontaneously, yields a light dry mass. This mass exhausted with hot alcohol affords a solution, which, on evaporation, leaves a crystalline substance having a light yellow colour, and presenting under the microscope an appearance similar to that of rock-candy. The crystals are slightly soluble in ether, more so in alcohol and chloroform, but quite insoluble in benzene, turpentine, and bisulphide of carbon. This substance does not possess the character either of an acid or an alkaloïd. It has little taste, on account of its extreme insolubility in the liquids of the mouth, but its solution in alcohol has the intensely acrid and sharp taste that characterizes recent cimicifuga.

J. B.

Some New Derivatives of Albumin. By O. Loew.†

After some preliminary remarks on our want of knowledge of the nearer derivatives of albumin, this paper describes some new bodies obtained from that substance.

By treating dried albumin with a mixture of concentrated nitric and sulphuric acids in the cold, and throwing the mixture, after standing for several hours, into cold water, a precipitate is thrown down, which, when dried, forms three-fourths of the albumin originally taken. It is a bitter, yellow powder, insoluble in water, alcohol, and dilute acids; soluble in dilute alkalies, forming a red solution, from which it may be reprecipitated unchanged. Assuming the formula of albumin to be $C_{72}H_{108}N_{18}SO_{22}$, the new substance is hexanitroalbuminsulpho-acid, $C_{72}H_{101}(NO_2)_6(SO_2OH)N_{18}SO_{22}$.

In order to determine whether this body is a true nitrous product, viz., one which, by the action of reducing agents, exchanges NO_2 for NH_2, or, on the other hand, belongs to that group of nitro-bodies which under like influences reproduce, like nitroglycerin and nitro-cellulose, the original substance,—in which, consequently, the hydrogen of the hydroxyl atoms is replaced by (NO_2), the latter supposition, on

* Pharm. J. Trans. [2], i, 866, from the American Journal of Pharmacy.

† Journ. f. prakt. Chem. 1870, 180.

account of the large number of hydroxyl molecules in albumin being as probable as the former: the hexnitroalbumino-sulphonic-acid was submitted to the action of ammonium sulphide in the first case, according to the author's view, a body of feebly basic properties would be produced; in the second, an albumino-sulphonic-acid would result. On performing the experiment the amidogen-groups replaced those of NO_2, but the new body had no basic, but rather feebly acid properties. *Hexamido-albuminsulphonic acid*, $C_{72}H_{101}(NH_2)_6(SO_2OH)N_{18}SO_{22}$, is a brownish-yellow powder, of faint taste, soluble in dilute alkalies. Concentrated alkalies decompose it, especially on warming, with strong evolution of ammonia. It swells up before dissolving in ammonia. Nitric acid exercises a powerful action, and dissolves it with evolution of red fumes. It is insoluble in dilute acids, but when freshly precipitated, is readily soluble in concentrated acids. With Millon's test, it does not react like the albuminates.

It is known that albumin swells up when placed in concentrated sulphuric acid, and then combines with the acid; but the nature of the compound formed has been hitherto unknown. Loew finds that albumino-sulphonic-acid, $C_{72}H_{107}(SO_2OH)N_{18}SO_{22}$, is formed. He describes it as a white powder, destitute of taste or odour, insoluble in dilute acids, soluble in dilute alkalies.

T. S.

Some Experiments with the so-called Peptones. By E. Brucke.*

The author gives the name of "peptone," as usual, to albumin which has been so far digested that it no longer gives a precipitate with potassium ferrocyanide, but is still precipitated by tannin. He finds that it is also precipitated by metatungstic acid, phosphomolybdic acid, and potassio-mercuric iodide. The author particularises two peptones—1. One soluble in alcohol and water, which he names *alkophyr;* 2. Another easily soluble in water but insoluble in alcohol, which he calls *hydrophyr*. They are both very similar to albumin, and have the same reactions, with the exception of the precipitation by potassium ferrocyanide, and the red coloration with sulphuric acid and sugar; on the other hand, they give a purple colour with cupric oxide and potash. 3. There is sometimes a third substance associated with the peptones, which gives the above-mentioned red coloration. The author obtained this substance by the artificial digestion of blood-fibrin, neutralization, evaporation, and extraction with alcohol, which dissolves this compound and leaves the hydrophyr undissolved. Neither Mulder nor Lehmann found anything insoluble in alcohol. The author believes that in their experi-

* Zeitschr. f. Chem. [2], vii, 61, from Wien. Acad. Ber., lxi, 250.

ments the digestion was carried much further, as he finds that there is always a portion insoluble in 96 per cent. alcohol, which at the commencement of the digestion is *hydrophyr*, but later, another compound which does not yield a purple colour with copper oxide and potash. In some albumin which had been submitted to artificial digestion for three months, there was no residue of *hydrophyr* insoluble in alcohol, but the solution contained *alkophyr*. Precipitated *hydrophyr* can be partially dissolved by treating it with acetic acid and alcohol. The author found that neither *alkophyr* nor *hydrophyr* was contained in albumin or in the gastric juice employed. In conclusion, the author states that the reaction with copper oxide and potash is a very delicate test for albuminous substances and peptones. A very small quantity of the cupric ammonia or potash solution, together with a little copper sulphate, is added to the albuminous or peptone substance, when the excess of copper oxide above that required for the production of the purple red compound falls to the bottom. The purple coloration is occasioned by the absorption of the green portion of the spectrum.

C. E. G.

Physiological Chemistry.

Effects of Change of Climate on the Human Economy. By ALEXANDER RATTRAY.*

Dr. RATTRAY contributes the results of several years' observations and experiments on the influence of tropical climates and other agencies, as diet, &c., on the human economy. The paper will hardly bear abstraction, as it consists for the most part of an elaborate series of tables with comments thereon.

With regard to the influence of tropical climates on the skin and kidneys, the tables show that the secretion of the functionally excited skin is greatly increased, while that of the kidneys and lungs is diminished. If, however, the drink be ample, and increased or diminished according to the temperature, the quantity of urine remains pretty uniform. It is not so much the nephritic as the cutaneous secretion which alters with variations in the amount of drink in the tropics, and in temperate climates the reverse.

Experiments as to the influence of tropical climates and diet on the body generally were made on the crew of H.M.S. "Salamander," numbering 209, of whom 91·86 per cent. were under 35, which may be

* Proceedings of the Royal Society, February 16th, 1871 (concluded from Proc. Roy. Soc., June 16th, 1870, p. 529).

considered the prime of life among seamen; while the whole were healthy.

The general result of Dr. Rattray's experiments is to show that a tropical climate causes loss of weight and general depression of both bodily and mental energy. When to this, other injurious influences are added, such as a diet of salt meat and hard work, there is noticed a progressive increase in the percentage of those who lose weight, according to the variety and intensity of the adverse agencies.

Taking as a standard of comparison life under the healthiest conditions, it is found that the percentage of those who lose weight is 9·5. A diet of salt meat increases this percentage to 19·69. Under a tropical climate it rises to 64·71. Under tropical climate (dry season) and a diet of salt meat combined, it rises to 65·22 per cent. In the rainy season the percentage is 76·34. When, in addition to this, hard subsolar work is undergone, it mounts up to 91·26 per cent.

The average gain and loss columns show a similar, though less regular, increase and decrease. Tropical climate is by far the most injurious influence, and its effects are materially aggravated by other adverse agencies. These facts apply both to junior and senior ages, though occasionally more apparent in the latter.

A change of climate is quickly followed by opposite results. Dr. Rattray considers that the general loss of flesh which results from the salt-meat dietary of long voyages, and is seen to be greatly intensified in and by tropical climate, is really the essence and primary stage of scurvy; while the intensity, obstinacy, and sometimes the origin of many other local and general diseases frequent among seamen, have doubtless an equally close alliance.

Several important hygienic and therapeutic suggestions are indicated.

T. L. B.

On the Effect of Diet and Exercise on the Elimination of Nitrogen. By E. A. Parkes.*

Dr. Parkes gives the results of three sets of experiments made on a remarkably healthy, powerful, and temperate young soldier. In the first set the man was fed on ordinary diet, whose amount and nitrogen-content was kept as nearly as possible constant. The periods of two hours each selected for rest and exercise were 12 or 14 hours after taking food, when the diet would have little influence on the urine excreted. Dr. Parkes formerly found that the outflow of nitrogen was slightly lessened during work, and slightly increased after it, while Karl Voit asserts that it is unaffected by exercise. The present experiments show

* Proceedings of the Royal Society, 1871, p. 349.

that exercise to the amount of 100-foot tons in two hours produces no marked change in the outflow of nitrogen by the urine. This result confirms Voit's assertion, but does not contradict Dr. Parkes' former experiments, as the amount of exercise in the present ones was much smaller.

The mean daily excretion of nitrogen by the fæces was 1·807 grm., with ordinary exercise, and 1·766 grm. when additional exercise was taken.

There was a slight decrease in the urinary water in the two hours of rest following two hours of exercise. Mental activity produced an increase in the water. After two hours of exercise, the pulse was 16 beats quicker than at a corresponding hour, when no exercise was taken, but it afterwards became slower, so that the mean pulse rate during the day was the same, whether the exercise were taken or not. This shows that the heart compensates itself for increased exertion by subsequent rest. Exercise made little difference in the temperature of the axilla and rectum.

In the second series, prepared food was given, so as to keep the amount of nitrogen introduced perfectly constant. It soon produced indigestion, the man lost weight, and the experiment was discontinued. Although the ingress was constant, the amount excreted varied much from day to day, but in five days was nearly equal to that ingested.

The third series was made with non-nitrogenous food, and was divided into two sets. The first set was made when the man had been well fed with nitrogen; the second when his body had become poor in it, from the use of concentrated food.

In the second set he did an extremely hard day's work on the fourth day, and on the fifth was quite well, and did not feel weakened from having been for five days on starch and butter.

Both sets show distinctly an increased elimination of nitrogen in the period of rest after severe exercise, confirming Dr. Parkes' former results, and supporting the statement of Liebig on this point, in opposition to that of Voit. Whether it was diminished during exercise or not was not clearly shown by the experiments. The non-nitrogenous diet for five days neither raised nor lowered the temperature in the rectum; it did not apparently affect his health, nor did it alter the frequency of the pulse, but the heart's action became weak, and the pulse soft. The experiments prove that force necessary for great muscular work can be obtained by the muscle from fat and starch, though changes in the nitrogenous constituents of the muscles also go on, which have as one effect an increased elimination of nitrogen after the cessation of the work.

T. L. B.

Experiments on the Influence of Food on the Production of Milk in the Cow. By GUSTAV KÜHN.*

SEVERAL series of experiments made at Möckern, in the year 1869, had led to the result that very considerable changes in the composition of the food might be made without inducing corresponding variations in the relative proportion of the constituents of the milk of the cow, the only variation being in the amount of concentration of the milk. The experiments of E. Wolff and Kreuzhage had led them to similar conclusions, though they seem at variance with experiments of a similar nature on other animals. To test these conflicting results, a series of experiments were made by the author in conjunction with Dr. A. Haase and Dr. H. Baesecke. Four cows were taken and fed, from January, 1870, onwards on a diet of moderate amount, not sufficient for the highest yield of milk. The food consisted of hay, barley-straw, and turnips.

At a subsequent date, the albuminous elements of the food were increased by the addition of bruised beans, which did not appreciably affect the non-nitrogenous elements of the food.

The increase of albuminoïds from about 0·9 kilogrammes in the first period to a maximum of 1·64 kilogrammes, was gradual in the case of cows I and IV, but sudden in the cows of II and III. (See Tables.)

In order to determine the influence of a partial increase of the fatty elements of food along with a rich albuminous diet, an addition of 0·5 kilogrammes of rape-oil was made in experiment 10 to the food of cow III. During the final period all the cows were fed for 7—8 weeks, on the same rations as at first, any slight difference that might exist being dependent on the degree of dryness of the food. The dry ingredients and fat of the mixed morning and evening milk of each cow were determined daily. The amount of casein, albumin, and sugar was determined every week, on four successive days, except the time between April 25 and May 8. When a change was made in the food, an analysis of all the milk-constituents was made in each case eight times, from the second to the eleventh day.

The method and duration of the individual experiments, the food proportions, and the variations in body-weight are seen in Table I. Observations on the amount and composition of the milk during the period when all the ingredients were determined, are given in Tables II—V. Table VI gives the mean composition of the milk during the whole period of each experiment, with the exception of the transition weeks.

The following methods of analysis were adopted :—

* Chem. Centralbl. 1871, 102.

For the determination of fat, the milk was mixed with some powdered marble, and evaporated to dryness over a water-bath under constant stirring. The gritty residue was dried, finely powdered, and extracted with absolute ether in tubes of about 1 cm. wide. Casein and albumin were determined according to Hoppe-Seyler's method. The mean of two analyses was always taken in reference to the above ingredients. In the determination of sugar by Fehling's solution, only one analysis was made each time.

TABLE I.

Animal.	No. of experiment.	Date 1870.	The food contained daily (in kilos.).					Weight of animal in kilogr.	
			Dry ingredients.	Proteids.	Non-nitrogenous extractive matters.	Fat (ethereal extract).	Cellulose.	At the beginning.	At the end.
I. Dutch cow, calved on 17/12 1869	1	—20/2	10·44	0·880	5·837	0·239	2·683	506	474
	5	21/2—13/3	11·66	1·249	6·533	0·259	2·770	474	473
	9	14/3—2/4	13·08	1·641	7·362	0·284	2·886	473	484
	12	3/4—13/5	10·74	0·902	5·998	0·245	2·768	484	447
II. Dutch cow, calved on 7/12 1869.	2	—20/2	10·44	0·880	5·837	0·239	2·683	495	480
	6	21/9—26/3	13·01	1·631	7·315	0·284	2·878	480	496
	13	27/3—13/5	10·71	0·899	6·015	0·242	2·733	496	472
III. Algäuer cow, calved on 19/12/69	3	—20/2	10·44	0·880	5·837	0·239	2·683	477	467
	7	21/2—13/3	12·91	1·621	7·232	0·282	2·875	467	479
	10	14/3—2/4	13·08	1·641	7·362	0·784	2·886	479	485
	14	3/4—13/5	10·74	0·902	5·998	0·245	2·768	485	485
IV. Voigtl. cow, calved on 19/12/69	4	—20/2	10·44	0·880	5·837	0·239	2·683	473	471
	8	21/2—13/3	11·66	1·249	6·533	0·259	2·770	471	473
	11	14/3—2/4	13·08	1·641	7·362	0·284	2·886	473	485
	15	3/4—13/5	10·74	0·902	5·998	0·245	2·768	485	472

TABLE II.—COW 1.

No. of experiment.	Date 1870.	Milk in natural condition.						Milk reduced to 12 p. c. dry contents.				
		Yield in kilogr.	Percentage composition.					Yield in kilogr.	Butter.	Casein.	Albumin.	Sugar.
			Dry ingredients.	Butter.	Casein.	Albumin.	Sugar.					
1	1—3/2	14·10	10·99	2·94	2·23	0·26	—	12·91	3·21	2·43	0·28	—
	8—10/2	13·11	11·08	3·02	2·20	0·30	4·74	12·11	3·26	2·40	0·33	5·13
	14—17/2	12·51	11·11	2·85	2·21	0·29	4·92	11·58	3·08	2·38	0·32	5·32
5	22/2	13·40	11·06	2·86	2·34	0·25	4·76	12·35	3·10	2·54	0·27	5·16
	23—24/2	12·98	11·03	2·84	2·30	0·23	4·66	11·93	3·09	2·51	0·25	5·07
	25—26/2	12·36	11·32	3·22	2·13	0·27	4·81	11·92	3·41	2·26	0·28	5·11
	1—3/3	12·51	11·57	3·46	2·15	0·25	5·07	12·11	3·59	2·23	0·25	5·25
	8—10/3	13·01	11·26	3·01	2·38	0·25	4·85	12·21	3·21	2·54	0·27	5·17
9	15/3	13·26	11·58	3·29	2·30	0·28	4·75	12·80	3·41	2·48	0·29	4·92
	16—17/3	12·98	11·44	3·13	2·37	0·28	4·88	12·38	3·28	2·49	0 29	5·12
	18—19/3	13·62	11·66	3·38	2·40	0·24	4·79	13·24	3·48	2 47	0·25	4·93
	22—24/3	12·96	12·01	3·60	2·39	0·25	4·91	12·97	3·59	2·39	0 25	4·90
	29—31/3	13·27	11·68	3·21	2·52	0·25	4·91	12·92	3·31	2·59	0·25	5·04
12	4/5	12·29	11·68	3·31	2·41	0·26	4·62	11·96	3·40	2·47	0·27	4·75
	5—6/4	11·27	11·55	3·24	2·40	0 27	4·71	10·85	3·37	2·49	0·27	4·89
	7—8/4	10·88	11·52	3·08	2·39	0·26	4·86	10·44	3·32	2·49	0·27	4·96
	11—13/4	10·53	11·53	3·31	2·32	0·27	4·87	10·12	3·45	2·41	0·28	5·07
	21—24/4	10·45	11·43	3·12	2·33	0·23	4·74	9·99	3·26	2·44	0·24	4·95
	11—13/5	9·64	11·13	2·99	2·32	0·24	4·75	8·95	3·21	2·50	0·26	5·11

TABLE III.—COW 2.

2	1—3/2	10·97	10·78	2·80	2·43	0·35	—	9·41	3·12	2·70	0·39	—
	8—10/2	9·81	10·66	2·63	2·36	0·38	4·64	8·72	2·96	2·67	0·43	5·23
	14—17/2	9·80	10·91	2·73	2·43	0·39	4·71	8·91	3·01	2·68	0·43	5·18
6	22/2	10·74	10·94	2·86	2·42	0·41	4·43	9·79	3·14	2·65	0·45	4·86
	23—24/2	11·21	10·98	2·78	2·48	0·36	4·21	10·26	3·04	2·71	0·39	4·60
	25—26/2	10·59	10·92	2·78	2·52	0·38	4·32	9 62	3·06	2·78	0·42	4·75
	1—3/3	10·18	10·83	2·73	2·47	0·37	4·45	9·18	3·03	2·73	0·41	4·93
	8—10/3	10·84	11·05	2·81	2·54	0·33	4 44	9·98	3·05	2·76	0·37	4·83
	15—17/3	10·93	10·92	2·80	2·46	0·36	4·46	9·95	3·07	2·70	0·39	4·89
	22—24/3	10·12	11·12	2·94	2·52	0·35	4·43	9·38	3·18	2·72	0·37	4·77
13	28/3	9·50	10·75	2·71	2·44	0·31	4·46	8·51	3·03	2·72	0·35	4·98
	29—30/3	9·08	10·72	2·67	2·44	0·33	4·55	8·11	2·99	2·73	0·37	5·09
	31—3/1/4	9·20	10·66	2·62	2·43	0·34	4·23	8·17	2·95	2·74	0·38	4·77
	5—7/4	8·62	10·70	2·67	2·41	0·35	4·25	7·69	2·99	2·60	0·38	4·76
	12—13/4	8·61	10·67	2·71	2·39	0·35	4·37	7·66	3·05	2·69	0·40	4·91
	21—24/4	8·56	10·58	2·62	2·34	0·32	4·28	7·55	2·97	2·68	0·35	4·85
	11—13/5	8·31	10·77	2·78	2·42	0·32	4·34	7·46	3·09	2·70	0·36	4·83

TABLE IV.—COW 3.

No. of experiment.	Date 1870.	Milk in natural condition.						Milk reduced to 12 p. c. dry contents.				
		Yield in kilogr.	Percentage composition.					Yield in kilogr.	Butter.	Casein.	Albumin.	Sugar.
			Dry ingredients.	Butter.	Casein.	Albumin.	Sugar.					
3	1—3/2	8·22	11·42	2·98	2·43	0·47	—	7·83	3·13	2·55	0·50	—
	8—10/2	6·97	11·55	3·14	2·38	0·59	4·37	6·71	3·29	2·47	0·61	4·52
	14—17/2	6·25	11·71	3·17	2·59	0·58	4·43	6·10	3·23	2·67	0·58	4·55
7	22/2	7·35	12·06	3·88	2·69	0·53	4·65	7·38	3·86	2·68	0·53	4·63
	23—24/2	7·69	13·13	3·30	2·66	0·50	4·49	7·77	3·26	2·63	0·49	4·47
	25—26/2	7·30	12·17	3·52	2·49	0·53	4·43	7·40	3·47	2·46	0·52	4·37
	1—3/3	7·76	12·20	3·47	2·62	0·52	4·65	7·89	3·40	2·58	0·51	4·57
	8—10/3	7·79	12·23	3·44	2·68	0·51	4·56	7·95	3·37	2·63	0·51	4·47
10	15/3	8·06	12·76	3·59	2·54	0·49	4·55	8·57	3·38	2·39	0·46	4·28
	16—17/3	8·21	12·42	3·67	2·66	0·53	4·60	8·51	3·54	2·60	0·52	4·45
	18—19/3	8·37	12·68	3·67	2·85	0·49	4·66	8·85	3·48	2·70	0·46	4·41
	22—24/3	8·15	12·50	3·51	2·72	0·50	4·61	8·49	3·36	2·63	0·48	4·45
	29—31/3	3·59	12·37	3·38	2·76	0·49	4·52	8·86	3·27	2·68	0·47	4·38
14	4/4	7·90	11·90	3·06	2·72	0·45	4·55	7·83	3·09	2·79	0·45	4·59
	5—6/4	7·53	11·80	3·11	2·61	0·47	4·36	7·40	3·16	2·65	0·47	4·47
	7—8/4	7·62	11·74	3·00	2·60	0·46	4·49	7·46	3·07	2·66	0·47	4·60
	11—13/4	7·35	11·84	3·09	2·64	0·46	4·67	7·25	3·13	2·67	0·47	4·73
	21—24/4	6·65	12·30	3·43	2·66	0·44	4·55	6·82	3·34	2·60	0·43	4·45
	11—13/5	5·93	12·55	3·98	2·73	0·49	4·52	6·20	3·53	2·61	0·46	4·31

TABLE V.—COW 4.

4	1—3/2	8·49	11·20	3·10	2·34	0·39	—	7·92	3·32	2·51	0·42	—
	8—10/2	8·54	11·26	2·94	2·46	0·37	4·66	8·02	3·13	2·62	0·40	4·97
	14—17/2	7·79	10·94	2·82	2·39	0·39	4·57	7·10	3·09	2·62	0·42	5·01
8	22/2	8·03	11·41	3·12	2·46	0·39	4·46	7·63	3·28	2·59	0·41	4·69
	23—24/2	8·21	11·27	3·03	2·37	0·36	4·30	7·71	3·23	2·53	0·39	4·58
	25—26/2	8·04	11·09	2·89	2·39	0·37	4·33	7·41	3·13	2·58	0·40	4·69
	1—3/3	7·99	11·18	3·02	2·40	0·36	4·31	7·45	3·24	2·58	0·40	4·62
	8—10/3	6·45	11·60	3·09	2·57	0·33	5·51	8·17	3·20	2·66	0·34	4·66
11	15/3	7·66	11·72	3·40	2·56	0·41	4·23	7·18	3·48	2·62	0·42	4·33
	16—17/3	8·17	11·72	3·23	2·69	0·38	4·46	7·97	3·31	2·75	0·39	4·57
	18—19/3	8·00	11·79	3·25	2·66	0·36	4·43	7·86	3·31	2·71	0·37	4·51
	22—24/3	7·60	11·70	3·18	2·57	0·38	4·43	7·41	3·27	2·64	0·39	4·56
	29—31/3	7·52	11·99	3·22	2·79	0·37	4·40	7·51	3·21	2·78	0·37	4·40
15	4/0	7·26	11·80	3·07	2·66	0·35	4·49	7·14	3·28	2·71	0·36	4·57
	5—6/4	7·08	11·62	3·12	2·61	0·37	4·40	6·85	3·21	2·69	0·38	4·54
	7—8/4	7·12	11·49	2·98	2·58	0·36	4·44	6·99	3·08	2·71	0·38	4·64
	11—13/4	7·13	11·53	3·20	2·61	0·37	4·39	6·94	3·29	2·68	0·38	4·51
	21—24/4	6·61	11·71	3·21	2·57	0·36	4·30	6·45	3·29	2·65	0·38	4·41
	11—13/5	6·55	11·39	3·11	2·55	0·37	4·23	6·22	3·28	2·69	0·38	4·46

TABLE VI.

Percentage composition of the milk after reduction to 12 p. c. dry contents.
(In the middle of the whole experiment, transition weeks excluded.)

Cow 1.	Butter. a.	Butter. b.	Casein.	Albumin.	Sugar.	Cow 3.	Butter. a.	Butter. b.	Casein.	Albumin.	Sugar.
Exp. 1	3·21	3·17	2·40	0·31	5·24	Exp. 3	3·23	3·22	2·57	0·57	4·54
„ 5	3·32	3·40	2·39	0·26	5·21	„ 7	3·36	3·39	2·61	0·51	4·52
„ 9	3·40	3·45	2·49	0·25	4·97	„ 10	3·31	3·32	2·66	0·48	4·41
„ 12	3·28	3·30	2·45	0·26	5·03	„ 14	3·34	3·33	2·62	0·45	4·49
Cow 2.						Cow 4.					
Exp. 2	3·04	3·03	2·68	0·42	5·20	Exp. 4	3·21	3·17	2·59	0·41	4·99
„ 6	3·08	3·08	2·73	0·39	5·86	„ 8	3·24	3·22	2·62	0·37	4·64
„ 13	3·01	3·01	2·67	0·37	4·83	„ 11	3·24	3·24	2·71	0·38	4·48
						„ 15	3·27	3·29	2·67	0·38	4·46

The general result of these experiments is to show that an increase in the albumin and fatty elements of a moderate diet produces an increase in the milk-yield, which gradually rises (along with bodily condition) to a certain maximum, corresponding in each case with the maximum increase of the above elements. Sooner or later, however, the natural diminution depending on the duration of lactation occurs, and no increase can be produced by increasing the food. Diminution of the above elements of the food causes a diminution in the milk-yield. The addition of fat increases the ingredients of milk generally, and has no special influence on the amount of fat in the milk. The absolute production of the individual elements of the milk agrees generally with the relative production of the milk as a whole (most regularly in the case of sugar). The variations from this are different for the different ingredients.

In the percentage numbers sugar does not appear to be affected by the diet. The variations in the amount of albumin are so small as not to be capable of determination. No influence on the amount of casein could be traced to the food. In one case there seemed even a diminution after an increase of the albuminoïd elements of the food. The influence of the food on the amount of fat is seen to be very small. When it appeared to be altered it was after increase of the albuminoïds of the food. Increase of the fatty elements of the food did not specially affect the amount of butter.—The variations in the percentage amount of casein and fat are to be attributed to irregularities in the fat production in the gland. In connection with this, compare Experiment 5 (Cow I).

The farmer must therefore not hope by variations in the food to produce a "butter-cow," or a "cheese-cow." The differences in this respect are differences of stock and individuals.

The experiments are being continued.

T. L. B.

On the Biliary and Urinary Pigments. By Dr. MAX JAFFÉ.*

1. THE well known colour-reaction produced by the action of nitric acid on the bile, is accompanied by characteristic spectroscopic changes. So soon as the blue tint appears, a broad, dark absorption band is seen, commencing between the C and D lines, but somewhat nearer D than C, and reaching to about the middle of the space between D and E. After some time this is resolved into two indistinct bands (α and β), separated by a clear space near D. As the reaction proceeds, these bands persist till the red tint is developed, but with gradually diminishing intensity. A little later than the advent of α and β, a third band γ makes its appearance between Fraunhofer's *b* and F lines, and almost exactly limited by F. Generally, as α and β become fainter, γ increases in intensity, and this is at its maximum towards the end of the reaction. The prolonged action of nitric acid, causes its disappearance.

2. The author having failed to obtain by Städeler's method a sufficiency of material for ascertaining the accuracy of that chemist's assertion, viz., that the blue pigment, giving Gmelin's reaction, is related to the quantity of indigo in the urine, made use of a new process for his investigation. An alcoholic solution of biliverdin or of bilirubin and ammonia, was decomposed with fuming nitric acid, the excess of acid being neutralized from time to time with ammonia, till it became blue, or till it clearly showed the bands α and β. The solution was then mixed with chloroform and precipitated by water. By this treatment all the colouring matter passed into the chloroform. The aqueous layer was quickly poured off, the chloroform solution washed repeatedly with water, filtered from the separated biliverdin, evaporated to dryness at the ordinary temperature, and the residue purified from traces of green pigment, by repeated solutions in chloroform. The substance thus obtained is, when freed from every trace of acid, not blue, but of a deep violet colour. It is insoluble in water, but soluble in alcohol, ether, and chloroform, forming beautiful violet solutions, which on the addition of the minutest trace of any acid, change to a splendid blue. If the acid be removed by washing, the original colour is restored; the addition of an alkali changes it to a brownish-violet. The acid solution exhibits the two spectroscopic bands α and β, as well as γ more or less clearly; whilst

* Arch. Pharm. [2], cxlv, 148.

the neutral and alkaline solutions are destitute of bands. The pigment dissolved in cold concentrated sulphuric acid forms a dark-green solution, which becomes turbid on the addition of water, from separation of green flocculi. These form with alcohol, a green solution, which reacts with nitric acid, and spectroscopically, like bile-pigment. When the flocculi are filtered off, the sulphuric acid solution is of a beautiful dark-brown colour in reflected, and of a violet colour in transmitted light; and viewed in the spectroscope has very much the appearance of a solution of indigo. It differs from this in the fact that when supersaturated with sodic carbonate, the solution turns brown, and undergoes no change when warmed with reducing agents; further, that the dried pigment yields no coloured crystalline sublimate.

The author does not attempt to decide whether the pigment described, is a simple substance, or a mixture, but adds, that if the action of nitric be allowed to go too far, the solution (as well as that in sulphuric acid) is not blue but violet, and shows (not the H_2SO_4 solution), the band γ with great clearness. If the sulphuric acid solution be shaken with ether, this acquires a red colour, and the blue colour of the acid is restored.

The pigment corresponding to the band γ may be obtained by the above method, if the action of the nitric acid be carried on till α and β have disappeared. It forms a brownish-red, probably impure powder, which is soluble in alcohol, ether, and chloroform, forming beautiful ruby-red solutions, which are reddish-yellow on dilution, and do not change colour on the addition of either an acid or an alkali. It is only the acid solution that gives the spectrum previously described.

3. By exhausting the bile of man or of the dog, or their alcoholic extracts, with dilute hydrochloric acid, a reddish or reddish-yellow filtrate is obtained, which exhibits a band coincident with γ, but much darker, and more sharply defined. On the addition of sodic hydrate, the colour changes to a bright yellow, and the band coincident with γ disappears, and is replaced by another narrower band δ, lying betwixt *b* and F, but nearer to *b* than F. If the solution be very faintly alkaline, both bands may be seen at the same time, and the addition of a trace of acid or of alkali determines the disappearance of the one or the other. If ammonia be used instead of soda, similar changes of colour are observed, but the band δ is very faint. On acidulation of the alkaline solution, the red colour, and the spectroscopic behaviour are restored, and a portion of the pigment can be withdrawn from the solution, by means of chloroform as a red powder, soluble in water, alcohol, and chloroform, precipitable by plumbic acetate, and by calcic chloride, from its aqueous solution. These precipitates when treated with acids, yield the original pigment.

The chloroform solution differs somewhat in its optical relations from

the watery and alcoholic solutions, in that the γ band lies in it a little nearer *b*.

4. The reactions of the pigment extracted from bile by hydrochloric acid show that it is probably identical with the normal colouring matter of urine. Urine examined by the spectroscope, without preliminary treatment, exhibits the γ band, but indistinctly. If the urine, however, be precipitated with lead acetate, and the precipitate decomposed by an acid, the filtrate shows this band much more clearly. When it is treated with sodium hydrate, a faint δ band comes out, and the chloroform solution shows the same characteristic displacement of its absorption-band as is described under 3. Whilst it is easy to confirm all the above reactions with the pale urine of healthy men, they are much more conspicuous with concentrated urine or with highly coloured red febrile urine. The spectroscopic peculiarities of the urinary pigment are not destroyed by boiling either with dilute mineral acids (nitric acid not excepted, if the action be not too prolonged), or with dilute alkalies. Jaffé found them unchanged in urine which had stood for a week, and was quite mouldy, but had not yet putrefied—a proof that the colouring matter of urine is not so readily decomposed as is commonly stated.

T. S.

On the Blood and Urine in Leukhæmia. By Dr. Reichardt.*

This paper contains copious references to the bibliography of the subject, and a summary of the results obtained by previous observers.

Scherer† found in the blood of a person suffering from leukhæmia, a gelatigenous substance; a body intermediate in properties between albumin and gelatin; hypoxanthine, previously discovered by him in the spleen, and by Gerhardt ‡ in the blood of the ox; and formic, acetic, and lactic acids, these having been also detected by him in the spleen. In a similar specimen of blood he also found hypoxanthine, leucine, and uric, lactic, and formic acids. § Folwarczny, ‖ following Scherer's method of analysis, detected in leukhæmic blood, only lactic and formic acids; but no acetic acid, gelatin, leucine, or hypoxanthine. Mosler and Körner ¶ extracted from leukhæmic blood, albumen, gelatin, and hypoxanthine, together with uric, formic, and lactic acids; but they were unable to detect acetic acid in it. The same experimenters subjected the urine in leukhæmia to chemical examination, but were unable

* Arch. Pharm. [2], cxlv, 142.

† Verhandl. d. phys.-méd. Ges. zu Würzburg, 1852, ii, 321.

‡ Ibid., 299.

§ Ibid., 1857, vii, 125; Arch. f. path. Anat. von Virchow, xxv, No. 2.

‖ Wien. Med. Zeitschr. 1858, No. 29—33.

¶ Virchow's Archiv. xxv, 142.

to detect anything abnormal in the relative proportions of the various urinary constituents. Finally, Mosler* made repeated analyses of the urine in splenic leukhæmia, and invariably detected hypoxanthine therein. Determinations of the other constituents, as uric acid, urea, &c., yielded no marked abnormal results.

Reichardt finds that in leukhæmic urine, urea and uric acid are abundantly present, but nearly in their normal relative proportions, the amount of uric acid, as compared with urea, being slightly increased—a fact often noticed before. The reaction of the urine was acid, and no albumin was present. The particular specimen of urine experimented with, was repeatedly examined for hypoxanthine, upwards of 400 c.c. being taken for each experiment, and both Scherer's and Körner's methods of extraction were tried, but the results were quite negative. A portion of the freshly drawn leukhæmic blood, after separation of the albumin, yielded gelatin and acetic acid, but no formic acid. The reactions for lactic acid were doubtful; and an albuminoïd body described by Scherer could not be detected. From another similar portion of blood (about 30 grms.), 0·123 grm. of gelatin was extracted, and 0·055 grm. of hypoxanthine. The identity of this latter substance was proved by its reactions with nitric acid and potash. This latter sample of blood, also yielded formic, lactic, and a doubtful trace of acetic acid; also a body first discovered by Theile, as a product of the action of potash upon albumin, to which the author assigns the name *albukalin*.

Theile, at that time Reichardt's assistant, in trying the action of potash on albumin and vitellin with a view to investigate the ammonias produced, found among the products, a body soluble with difficulty in absolute alcohol, but readily soluble in alcohol of 90 per cent. This substance amounted to 12 or 15 per cent. of the vitellin taken. When dried, it formed a friable brown mass, which burnt with the odour of an albuminous body. When dried in thin layers, it exhibited under the microscope, regular crystals, like the well known efflorescence of sal ammoniac; but it was proved that no ammonia was present.

Theile found this body to be free from sulphur, and he obtained the formula $C_4H_8NO_3.\frac{1}{2}H_2O$, which says Reichardt, approximates to that of glycocine, $C_2H_4NO_2$; and he thinks it probable that albukalin, as a product of the action of potash on albumin, bears the same relation to this body, as glycocine to gelatigenous substances.

Besides the crystalline form, Theile obtained the following distinctive reactions.—The aqueous solution has a faintly acid reaction. It yields with cupric sulphate, a deep emerald-green coloration, but no precipitate. With silver nitrate, it gives a white flocculent precipitate, speedily becoming brownish-violet; with platinic chloride, a yellow flocculent

* Virchow's Archiv. xxxvii, 43.

precipitate; and with mercuric nitrate, a very voluminous, flocculent, white precipitate. Sodium hydrate causes, after some time, a white precipitate.

Similar reactions were obtained with the before-named substance obtained from the blood of a leukhæmic person, the presence of ammonia being excluded. The residue from the distillation of the blood with sulphuric acid, when neutralized with calcic carbonate, left on evaporation, instead of the characteristic crystals of calcium lactate, cubical crystals, which, after repeated crystallisation, changed into the above mentioned crystals resembling sal ammoniac, and giving, as already stated, all the reactions for albukalin.

Since albukalin forms a considerable portion of the products of the decomposition of albumin or vitellin by potash, it is probable that it is often present in the animal fluids, in the same manner as other well known bodies, as leucine, tyrosine, &c. This requires further investigation. T. S.

Urea, a normal and constant Constituent of Bile. By O. Popp.*

When bile is diluted with an equal volume of water and treated with lead acetate, completely saturated with lead oxide, the filtered liquid treated with sulphydric acid, again filtered and evaporated on the water-bath, and the residue exhausted with absolute alcohol, a solution is obtained, which leaves urea on evaporation. The bile of the pig seems to contain more urea than that of the ox.

F. H. H.

Sarcolactic Acid in Urine. By Th. Simon and F. Wibel.†

The urine of a patient suffering from trichinosis in the Frankfort Hospital, when treated according to known methods, yielded a considerable quantity of sarcolactic acid as zinc-salt, recognisable by its external characters and its solubility in alcohol. An analysis, made with a small quantity of the salt, led to the following numbers:—

	Calculated.	Found.
Zn	23·29	23·12
$2(C_3H_5O_3)$	63·81	65·99
$2H_2O$	12·90	10·89

As the zinc-salt of fermentation lactic acid contains 3 mol. of water, the above salt is evidently sarcolactate.

J. R.

* Zeitschr. f. Chem. [2], vii, 88; from Ann. Ch. Pharm., clvi, 88.

† Deut. Chem. Ges. Ber., iv, 139.

Analysis of a Sub-Fossilised Human Thigh-Bone from an Ancient Grave at Ohlsdorf. By F. WIBEL.*

ANALYSIS gave 12·52 per cent. of organic substance, 74·99 per cent. of calcium phosphate with traces of magnesium phosphate and calcium fluoride, 5·48 per cent. of calcium carbonate, 7·01 per cent. of salts and impurities, and 1·82 per cent. of nitrogen.

The author considers that the above numbers support the view put forward by him some time ago as to the determination of the age of bones by their composition, the analysis agreeing very closely with that of a thigh-bone from another grave of the same period—the so-called "bronze age." J. R.

On an Enormous Proportion of Earthy Matter in a Human Lung. By E. VON GORUP-BEZANEZ.†

OF late years the attention of pathologists has been directed to the diseases of the respiratory organs which prevail among certain classes of workmen, from the inhalation of various kinds of dust while following their occupation. It was long a disputed question whether the particles of oxide of iron, silica, &c., thus inhaled merely lodged within the air cells of the lungs, or penetrated through their walls into the tissue between them; but this has at last been decided in the affirmative by Professor Zenker. On examining the lung of a woman who had been exposed to the dust of iron oxide used in preparing books for gold-leaf, he found the powder in the tissue between the air-cells and in their walls, as well as in their cavities. From 57 grms. of this lung Gorup-Bezanez obtained no less than ·828 grm. of iron oxide. Supposing that it was equally distributed throughout both lungs, the amount contained in them could not be less than from 21 to 22 grms.

In another lung, that of a workman exposed to the dust of a mixture used in preparing ultramarine, he found a considerable amount of silicate of alumina, quartz sand, and more oxide of iron than normal, 227 grms. of lung yielding 3·1925 silicate of alumina, 0·3298 quartz sand, and 0·329 iron oxide. Supposing it to be equally distributed through both lungs, and estimating their weight at 1,500 grms., they would contain no less than 29·86 grms. of earth and sand.

T. L. B.

On the Excrement of the Common Bat.‡

ACCORDING to Popp's researches, the excrement of the Egyptian bat contains 80 per cent. of crystallised urea, and is hence manifestly the

* Deut. Chem. Ges. Ber. iv, 138.
† Ann. Ch. Pharm., clvii, 287.
‡ Ann. Chem. Pharm., clviii, 115.

urine of the animal. It is not ascertained what becomes of the fæces. Since the question possesses some physiological interest, Kopp has investigated the excrement of the common European bat (*Rhinolophus Hipposideras*), procured by Professor Ehlers from material from a locality where it had collected to the thickness of three inches.

This excrement was in the form of dry, small, long, granular masses, of a dark brown colour, and was obviously composed of the fæces of the animal intermingled with the decomposition-products of the urine, viz., ammonia salts. It contained not a trace of urea, and no uric or oxalic acids. The chief portion seemed to be made up of the undigested wing-cases of insects. Cold solution of soda extracted a brown humus-like body, with abundant evolution of ammonia. Dried at 100° the excrement yielded 8·25 per cent. of N., and 6·25 per cent. of ash, containing potassium, sodium, calcium, magnesium, ferric oxide, chlorine, sulphuric, silicic, and phosphoric acids—36 per cent. of this last.

Why the urine of the Egyptian bat is free from fæces is undetermined. The dryness and warmth of the climate account for the non-decomposition of the urea.

T. S.

Analysis of an Earthball and Intestinal Calculus from the Horse.
By James F. Stark.*

The earthball analysed was 5 inches in diameter, and weighed over 2 lb. It was composed of alternate layers of mineral matter, and of mineral matter intermingled with substances of organic origin. A fair average sample gave:—

MgO.	NH_3.	P_2O_5.	H_2O. (combined).	
13·59	8·83	24·11	36·68	= 83·21

CaO.	Al_2O_3.	Fe_2O_3.	Na_2O.	P_2O_5.	CO_2.	SO_3.	SiO_2.	NaCl.	Organic matter.	
0·24	4·17	1·03	0·36	0·19	0·02	0·47	5·20	0·48	4·69	= 16·85
										100·06

The chief feature in this analysis is the large proportion of ammonio-magnesic phosphate present.

The calculus, 1 inch in diameter, gave—

Ammonio-magnesic phosphate	98·229
Organic matter, soluble in hydrochloric acid ..	0·801
" insoluble " " ..	0·900
Silicic acid	0·044
	99·984

T. S.

* Chem. News, xxiii, 199.

On the Flesh-juice of Phocæna communis. By OSCAR JACOBSEN.*

THE object of this paper was to compare the flesh-juice of a marine mammal with that of other mammals. For this purpose, 10 kilogrms. of the flesh of a young porpoise, free from fat, were treated in a manner essentially the same as that which Limpricht applied to horse-flesh. The amount of the ingredients (exclusive of the potassium chloride and calcium and sodium salts present) per 10,000 parts is given, together with the result of a similar examination of horseflesh:—

	Porpoise flesh.	Horseflesh.
Creatine	6·10	7·60
Sarcine (hypoxanthine)	1·05	1·28
Xanthine	traces	0·11
Inosite	0·08	0·30
Sarcolactic acid	7·45	4·47
Taurine	—	0·70

Dextrin and inosite occur in the lungs of the porpoise.

W. H. D.

Researches on Alcoholic Fermentation, and on the Mode of Nutrition of the Yeast-plant. By ADOLPH MAYER.†

AFTER a long preliminary statement, the author proceeds to give the results of his own experiments, although he does not, for want of space, give the experiments themselves on which his conclusions are founded. He concludes:

That the acid potassium phosphate is the salt most intimately related to the proper physiological function of yeast—the conversion of sugar into alcohol and carbon dioxide—since the exclusion of that salt exerts immediately, and directly, an injurious effect upon the fermentative process. This salt cannot be replaced by the sodic or ammonic phosphates, or by any other salt of potassium.

Other salts are, however, necessary to the complete nutrition of the yeast-plant. If a mixture of water, sugar, and an appropriate nitrogenous body, in proper proportions, be taken, and no mineral constituent except potassium phosphate be added, fermentation sets in actively, after the addition of a very small quantity of yeast, but after a time the yeast-cells will be found to be incompletely formed, and they are no longer capable of keeping up vigorous alcoholic fermentation.

The salts which prevent this degeneration of the yeast-plant, and so must be regarded as food for it, are those of magnesium, although these stand in no direct relation to the decomposition of the sugar.

* Ann. Ch. Pharm., clvii, 227.

† Pogg. Ann. cxlii, 293.

The minutest quantity of sulphur suffices for the nutrition of the yeast-plant, and this substance appears to be present even in the purest sugar-candy. All the other constituents of the ashes of the plant bear no relation to its nutrition, and calcium may be entirely removed without injury.

These results show that the requirements of the yeast-plant are much simpler than those of the higher plants and animals. Iron, for instance, and probably calcium, may be completely absent from growing yeast. It is also manifest that the several functions of plants demand specific forms of nutriment for their due performance.

With regard to the nutrition of yeast by nitrogenous substances, the following results were obtained. They are somewhat different from those commonly received. The albuminous, and many other highly organized bodies, are ill-adapted for the nutrition of the yeast-plant. Ammonium salts, and nitrogenous organic substances similar in constitution to ammonia, are quite competent to the nutrition of the yeast-plant; but this plant differs from the higher vegetable organisms in that it is incapable of deriving the chief portion of its nitrogen from the nitrates. Pepsin was found to be the best food for yeast, and the diastase of beer was also found to be a good nitrogenous substance for this purpose, and for supporting vigorous alcoholic fermentation; but with respect to diastase, it was found that this in no way depended upon the facility with which that body ferments, for previous heating of the fluid to the boiling point exercised no influence on the subsequent fermentation by means of yeast.

It was ascertained that during alcoholic fermentation yeast not only decomposes sugar into alcohol and carbon dioxide, but that the organism secretes unknown nitrogenous substances which are no longer capable of affording nourishment to the plant.

Speaking of the connection between the nutrition of the yeast-plant and alcoholic fermentation, the author says that yeast does not require the access of free oxygen for its growth, and differs in this respect from other vegetable organisms; it does not *breathe* in the same sense as the higher plants, animals, and even other fungi do. The dictum that every organism, in order to furnish manifestations of life, must appropriate oxygen, cannot, therefore, be unreservedly admitted, and he proposes to substitute for it the following:—that for the completion of the manifestations of vitality in every organism, chemical forces must come into play, and that such chemical forces are transmuted into heat and mechanical motion; further, that the chemical force derived from the affinity for oxygen of organic substances in plants must be considered as a special case of the above general law, although the most common one. If this modification of the generally received theory be admitted, the vital changes undergone by yeast in a saccharine solution may be classed with those changes of matter which take place in the higher

organisms, and at the same time the series of phenomena taking place during the growth of the yeast-plant become explicable. The splitting up of a carbohydrate into alcohol and carbon dioxide is accompanied by a loss of chemical force—the alcohol formed has a much smaller thermic equivalent than the sugar from which the alcohol was formed. The case is one of internal combustion (*innere Verbrennung*). Moreover, the formation of cellulose in the cell-wall of the newly formed yeast plant is a case of splitting up of sugar into more highly and less oxidised products, and during the process there is a consumption of chemical force. The connection between the splitting up of the sugar and the budding of the yeast-plant is thus indicated with much probability. T. S.

Agricultural Chemistry.

On Chemical Substitution in Plants. By RUDOLPH STROHECKER.* IN June, 1857, Otto Sendtner collected specimens of *Fontinalis antipyretica* growing in the small river Ohe, in the Bavarian forest, and forwarded them, with a sample of the water, to Wittstein for analysis. In September in the same year, specimens of the same plant were taken from the river Isar, and also analysed. The composition of the two river waters, and that of the ash of the plants taken from them were as follows:—

	Water from the Ohe.	Water from the Isar.	Fontinalis antipyretica.	
			From the Ohe.	From the Isar.
	Solid contents. ·016 per cent.	Solid contents. ·225 per cent.	Ash. 22·60 per cent.	Ash. 9·88 per cent.
K_2O	9·005	1·832	·460 }	2·767
Na_2O	·424	2·907	1·928 }	
CaO	2·963	34·737	2·755	18·150
MgO	1·056	6·982	1·133	5·498
Fe_2O_3	·237	·133	17·039	9·910
Al_2O_3	·108	—	9·272	1·616
Mn_3O_4	—	—	4·555	·850
SO_3	1·165	12·368	1·648	2·827
P_2O_5	3·360	·115	trace	5·962
Cl	1·088	·439	·210	·506
SiO_2	7·238	1·029	61·000	51·494
CO_2	—	21·981	—	—
Organic matter	73·601	17·576	—	—
	100·245	100·099	100·000	99·580

* Arch. Pharm. [2], cxlv, 131—149.

Wittstein concluded from these results that the proportion of ash constituents of a plant is influenced by the character of the medium in which it grows. Nägeli disputed the correctness of this deduction, and thought the different composition of the plants was due to difference of age, and admixture of foreign matter. In reply, the author states that the plant from the Isar was freed from foreign matter by washing with acetic acid, but admits that there was a difference of age, as indicated by the larger proportion of mineral matter in the younger plants from the Ohe.

Mulder, in 1863, ascertained that cellulose combines with metallic oxides, and that isomorphous bases can replace each other in such combination. There is in fact every probability that isomorphous bodies, as As_2O_5 and P_2O_5, which replace each other in inorganic compounds, should do the same in organic compounds.

Replacement of bases appears in some cases to influence the form of a plant. At Heidelberg the leaves of the *Hieracium boreale* have a different angular dentation if growing on the calcareous Muschelkalk, than when grown on the magnesian soil of the Bunter sandstone.

For Pharmaceutical purposes, the possible effect of difference of soil on the qualities of a plant should be borne in mind. R. W.

Analytical Researches upon Rocks, with reference to their Constituents absorbable by Plants. By C. Kosmann (Arch. Sc. phys. nat. [2], xl, 153).

On the Ash-constituents of the Seeds of the Egyptian Acacia nilotica and Hibiscus esculentus. By O. Popp.*

The *Acacia nilotica*, the Lebbach of the Arabs, is an arborescent leguminous plant, common in Egypt, especially in the neighbourhood of Cairo, and, together with the *Ficus Sycomarus*, much used for planting in the streets. It produces innumerable leathery pods, which ripen in March. The seeds, when quite ripe, are extremely hard and horny; dried at 110°, they yielded 5·3 to 5·5 per cent. of nitrogen. Being similar in composition to beans and peas, these seeds might probably be used for food. They become soft by soaking in hot water. The unripe pods yielded 1·8 to 2·0 per cent. nitrogen; the ripe pods, 1·0 per cent. The ash of the pods was rich in potassium, sodium, and magnesium.

The *Hibiscus esculentus* belongs to the malvaceous order. It is called in Egypt *Bammyé*, and is cultivated as a garden vegetable, the unripe green fruits being cooked in a similar way to our green beans. The fruit dried at 100° contained 2 to 2·4 per cent. nitrogen. Like other members of the same family, it is rich in pectin, starch, and mucilage. The ash contains abundance of potash, soda, magnesia,

* Arch. Pharm. [2], cxlv, 140–142.

phosphoric acid, sulphuric acid, and chlorine. The ripe seeds contained 2·4 to 2·5 per cent. nitrogen.

The ash analysis of the seeds of both plants gave as follows:—

	Acacia nilotica.	Hibiscus esculentus.
K_2O	33·388	38·842
Na_2O	5·360	4·576
CaO	14·212	7·813
MgO	12·103	12·021
Fe_2O_3	·612	·861
P_2O_5	16·229	24·690
SO_3	3·650	·561
SiO_2	1·809	·747
Cl	·345	1·537
CO_2	12·112	8·252
	99·820	99·900

R. W.

Effects of the Drought of 1870 on some of the Experimental Crops at Rothamsted. By J. B. LAWES and J. H. GILBERT.*

THE authors experimented in 1849 and following years on the amount of water given off by plants during their growth. This was found to bear relation to the amount of dry matter or carbon, but not to that of nitrogen, fixed. Thus, in the growth and ripening of graminaceous and leguminous corn crops, from 250 to 300 parts of water are given off for 1 part of dry substance produced, whilst that of the leguminous may contain 2 or 3 times as much nitrogen as that of the graminaceous crop. A crop of wheat or grass, yielding $2\frac{1}{2}$ tons of dry matter per acre, may consequently have evaporated 750 tons of water, the latter crop by the end of June, the former by the end of July.

The total rainfall at Rothamsted in April, May, and June, averaged over 15 years 6·56 inches, but in 1870 it was only 2·79 inches; the amount of hay per acre produced on three of the experimental plots in this season is given below. The plots had been manured in the same manner for 15 years:—

	Average produce, 1856–70.	Produce in 1870.	Deficiency in 1870.
	cwts.	cwts.	cwts.
No manure	$22\frac{3}{4}$	$5\frac{3}{4}$	17
Cinereal manure and ammonia salts	$52\frac{2}{3}$	$29\frac{1}{2}$	$22\frac{7}{8}$
Cinereal manure and nitrate of soda	$57\frac{2}{3}$	$56\frac{1}{4}$	$1\frac{5}{8}$

* Journ. Roy. Agricultural Soc. [2], vii, 91.

In the early years of the experiment, the ammonia salts gave a larger crop than the nitrate of soda; in the later years this was reversed. In 1870 the nitrate of soda plot appears to have been scarcely affected by the drought, and yielded a far greater crop than the ammonia salts supplying the same amount of nitrogen. Reckoning an inch of rain at 101 tons per acre, the crop by nitrate of soda must have evaporated 700 tons of water. The whole rain-fall in the three months of active growth amounted to only 282 tons: how, then, did this plot obtain its water supply?

Samples of the soil were taken, after the removal of the crop, at various depths, extending to the extreme range of the roots, and the percentage of moisture determined at 100° H., with the following results:—

	No manure.	Cinereal manure and ammonia salts.	Cinereal manure and nitrate of soda.
First 9 inches.....	10·83	13·00	12·16
Second 9 inches.....	13·34	10·18	11·80
Third 9 inches	19·23	16·46	15·65
Fourth 9 inches.....	22·71	18·96	16·30
Fifth 9 inches.....	24·28	20·54	17·18
Sixth 9 inches.....	25·07	21·34	18·06
Mean	19·24	16·75	15·19

The two manured plots contain more moisture in the first 9 inches than the unmanured soil, but from this point downwards they contain far less; the soil of the nitrate of soda plot being much the driest. Reckoning the soil, exclusive of stones, as weighing 1,000,000 lbs. per acre for each 3 inches depth, it appears that the nitrate of soda plot contained to a depth of 54 inches 325 tons less water than the unmanured plot; a result indicating that the nitrate crop had removed at least 325 tons more water from the soil than the unmanured crop. Examination also showed that the soil of the unmanured plot was altered by vegetation to a depth of about 18 inches; that manured with ammonia salts to about 36 inches; while that manured with nitrate of soda was more or less disintegrated to a depth of 54 inches. Nitrates being far more diffusible in soil than ammonia salts, are doubtless washed to greater depths, where the roots follow them. It is observed at Rothamsted, that nitrate of soda has generally a disintegrating effect on the soil, which is there a heavy loam. The herbage upon the three plots was in each case distinct in character, the result of repeated application of the same manure. With ammonia salts, *Dactylis glomerata* and *Agrostis vulgaris* were the most prominent grasses; with nitrate of soda, the

deep-rooted *Bromus mollis* formed one-half the crop, and *Poa trivialis* was abundant; with no manure, the number of species was largest, none were vigorous. The more disintegrated condition of the soil, favouring capillary attraction, and the deep-rooted character of the herbage, account for the comparative independence of external supply of water shown by the nitrate crop.

In the very dry summer of 1868, samples of soil were taken, at the end of July, from three plots in the experimental wheat field, to a depth of 36 inches; there was little difference in the moisture of the three plots. That with no manure averaged 12·44 per cent.; that receiving cinereals and ammonia salts, 12·95 per cent.; that receiving farmyard manure, 11·04 per cent. The soils of the same plots were again sampled in the following January, after heavy rain. In the first foot the difference was most striking, the unmanured soil containing 22·93 per cent. water; that manured with cinereals and ammonia, 23·54 per cent.; that manured with dung, 32·02 per cent. The respective water-holding power of the soils is shown below.

Tons of Water per Acre, to a depth of 36 inches.

	July, 1868. Dry.	January, 1869. Saturated.	Difference.
No manure	666	1396	730
Cinereals and ammonia salts	694	1549	855
Farmyard manure	591	1610	1019

The effect of continued manuring in increasing the water-holding power of the soil is very evident. The drains in the dunged plot scarcely ever run, though free from obstructions. It is clear that on both the manured plots the crop had a greater amount of water at command than the crop on the unmanured soil.

In the summer of 1870 samples were also taken from soil growing barley, and from uncropped land in the immediate neighbourhood. The following were the percentages of water found:—

	Fallow land, June 28, 1870.	Barley land, June 28, 1870.
First 9 inches	20·36	11·91
Second 9 inches	29·53	19·32
Third 9 inches	34·84	22·83
Fourth 9 inches	34·32	25·09
Fifth 9 inches	31·31	26·98
Sixth 9 inches	33·55	26·38
Mean	30·65	22·09

Calculation shows that the barley land contained about 900 tons less water per acre than the fallow land.

A comparison of the different experimental crops at Rothamsted shows that grass generally suffered most from the drought, barley considerably, and wheat least; grass with nitrate of soda, and barley with farmyard manure, being marked exceptions.

It may be assumed that a good crop of hay, wheat, or barley, will exhale 7 inches of rain while growing; in what proportion is the remaining rainfall disposed of by evaporation and drainage? Dr. Dalton, experimenting three years (1796–8) with a cylinder 3 feet deep, filled with earth and sunk in the ground, found the drainage 25 per cent. of the rainfall. Mr. Dickinson, experimenting eight years (1836–43) with a similar apparatus, but under conditions of freer drainage, found that $42\frac{1}{2}$ per cent. of the rainfall passed through. In both experiments grass grew on the top of the cylinder. Investigations on the subject have been lately commenced at Rothamsted. Three drain-gauges, each of $\frac{1}{1000}$th of an acre in extent, have been established by carefully undermining the soil at depths respectively of 20, 40, and 60 inches. With a rain-fall of $10\frac{1}{2}$ inches in the last four months of 1870, about 50 per cent. passed 20 inches, about 40 per cent. passed 40 inches, and about 20 per cent. drained beyond 60 inches from the surface.

The drainage water collected in the winter at Rothamsted, from land receiving ammonia salts (equal to 82 lbs. nitrogen per acre) the previous autumn, has been found by Drs. Frankland and Voelcker to contain $2\frac{1}{2}$ to 3 of nitrogen per 100,000. At this rate each inch of rain passing beyond the reach of the roots occasions a loss of about 6 lbs. of nitrogen per acre.

R. W.

On Sugar-Beets and Beetroot Distillation. By A. Voelcker.*

The existence of crystallisable sugar in beetroot was first noticed in 1747 by Marggraf of Berlin; the manufacture commenced about 1809 under the auspices of Napoleon I. There are at present on the continent nearly 2,000 beetroot-sugar factories and distilleries, chiefly French, North German, and Belgian, producing in the year 1869–70 689,500 tons of sugar. The manufacture of beetroot-sugar was introduced into England three years ago by Mr. Duncan, of Lavenham, Suffolk, and the distillation of beet-root spirits is carried out on a large scale by Mr. R. Campbell, at Buscot Park, Berks.

Numerous analyses of sugar-beets grown in England and Ireland are given by the author. The season of 1870 proved more favourable

* Jour. Roy. Agricultural Soc. [2], vii, 60.

to the formation of sugar than 1869. Samples grown in 1869 gave—English roots, 8—12 per cent. sugar; Irish roots, 6—11 per cent. sugar. Samples of the crop of 1870 gave—English roots, 9—13·3 per cent. sugar; Irish roots, 10—14·8 per cent. sugar. Large roots are shown to be more watery, and contain less sugar than smaller roots. Liberal manuring increases the bulk of the crop but injures its quality, one effect being the increase of albuminous and saline matters, the presence of which prevents the crystallisation of a certain percentage of the sugar. The part of the root grown above the ground contains less sugar and more nitrogen than the buried portion; hence the utility of deep culture of the soil. The following are characteristic analyses:—

	Lavenham, 1869. Average of fifteen lots.	Large root from Buscot, 1869.	Single root, Berkshire, 1869.		Viewmont, Kilkenny, 1870. Average of ten roots.
			Upper portion.	Lower portion.	
Water	82·46	91·50	87·20	86·05	77·76
Sugar	11·06	3·89	4·24	8·05	14·73
Albuminous compounds	·81	1·04	2·39	·82	1·66
Pectin, &c.	·66	·36	·40	·89	·69
Crude fibre	3·87	1·90	3·73	3·08	4·36
Ash	1·14	1·31	2·04	1·11	·80
	100·00	100·00	100·00	100 00	100·00
Weight	..	12·25 lbs.	·31 lb.	2·5 lbs.	1·53 lbs.

The distillation of spirit from beetroot is largely practised on the Continent; it has been recently commenced in England on a great scale by Mr. Campbell, of Buscot. This manufacture turns to profit the molasses of the sugar factories, and utilizes the crops of bad seasons, when the percentage of sugar is below that (about 8 per cent.) required for profitable extraction. It is considered by many more remunerative than the manufacture of sugar, and is certainly more consistent with high farming, the albuminous and saline matters favoured by liberal manuring being no obstacle to the production of spirit.

Beetroot is prepared for fermentation by one of three processes:—I. The roots are pulped or sliced, mixed with a small quantity of sulphuric acid, then pressed, and the juice fermented. II. (Champonoi's method.) The roots are sliced, and treated with hot wash acidulated with sulphuric acid; no press is used, the sugar being extracted

by displacement. III. (Leplay's method.) The slices of beetroot are placed in vats, and fermented without previous treatment. The residual pulp from each of these methods is used as cattle food.

Beetroot spirit is very apt to be contaminated with fusel oil, but the use of first-rate distilling apparatus (as that of Messrs. Savalle) effectually removes this impurity.

Since sugar-beet contains far more nutritive matter than the best mangolds, it may frequently be of more value for feeding purposes than for the sugar or spirit manufacture.

R. W.

On Mulberry Leaves from Turkestan, by Dr. E. Reichenbach; *and on the Silk-worm Disease*, by J. v. Liebig.*

In this paper a long description of the various sorts of mulberries met with in Turkestan is given. The amount of nitrogen in the leaves was alone determined, and was found to average 3·73 per cent., varying from 3·38 to 4·05 per cent., whilst Japanese and Chinese leaves contain 3·29 and 3·13 per cent. respectively.

Calculated as protein bodies, the nitrogen in the leaves from Turkestan corresponds to between 211 and 253 lb. of protein subtances per 1,000 lb. of leaves. These amounts are sufficient to support the silk-worms during the production of silk, and the great amount of nutritive matter in the Turkestan, and also in the Japanese and Chinese leaves, accounts for the fact that the silkworm disease has never appeared to any extent in Turkestan, and that the Japanese, Chinese, and Turkestan silks are the best.

Liebig agrees with the view taken by the author of the paper just noticed, in attributing the occurrence of the silk worm disease in Europe to deficiency of nitrogenous matter in the mulberry leaves, resulting from want of care in the cultivation of the trees. In China, Japan, and Turkestan, where the disease among the worms is almost unknown, the mulberry trees are treated like vines; they are carefully pruned and manured. In Italy and France, on the other hand, they are treated with scarcely more care than forest trees.

Fungi, which are usually regarded as the cause of the silkworm disease, merely find in ill-nourished animals the soil most suited for their development.

The eggs of healthy and vigorous parents will produce healthy worms, which, even when fed on food poor in nitrogen, produce silk, although they may not attain to the same development as better nourished caterpillars. If, however, an insufficient store of silk-producing material is accumulated in their bodies, other of their bodily

* Ann. Chem. Pharm., clviii, 92.

constituents must be used to supply the want. Such an appropriation must naturally produce a disastrous effect upon their propagation and their products. The eggs of such worms cannot have the same properties as those of animals that are better nourished. Experience shows that caterpillars raised directly from Chinese and Japanese eggs, and fed on defective food, produce silk; but the second generation reared from the imported eggs, even when fed on the same food, perishes from the disease, generally, before the spinning of the cocoons. It is manifest that if the disease depended upon external causes, these would affect both the first and second generations equally.

T. S.

Analytical Chemistry.

On a New Volumetrical method for determining Sulphuric Acid, Baryta, Chlorine, Bromine, and Iodine. By E. Bohlig.*

This method is based upon alkalimetrical principles. Alkaline sulphates are known to be partially decomposed, in contact with baric carbonate, into alkaline carbonates and barium sulphate. The decomposition is complete in the presence of free carbonic anhydride; acid carbonates of the alkali-metals are left in solution, together with some acid baric carbonate, which can be removed by boiling. The solution is filtered, and the alkaline carbonate determined by means of a standard acid solution, and the amount of sulphuric acid or alkaline sulphate calculated from the amount of normal acid required.

Neutral chlorides, bromides, and iodides, more especially of the alkali-metals, are most readily decomposed by pure silver oxide into insoluble silver salts, leaving the alkali-metal in solution as hydrate (ammonia salts always excepted) which can then be determined as usual by standard acid.

The author treats solutions containing sulphates of the heavy metals, of the earths or alkaline earths (lime), and free from acids whose presence would influence the method, viz., phosphoric, arsenic, oxalic, &c., with a solution of potassic carbonate so as to precipitate the bases and leave about double or treble the amount of alkaline carbonate in solution. From 1 to $1\frac{1}{2}$ grm. of substance is operated upon in a flask. The solution is made up to 500 c.c. well shaken, and the precipitate allowed to subside. 50 c.c. are then filtered into a porcelain dish and

* Arch. Pharm. [2] cxlv, 113.

heated to boiling, and standard acid (HCl) added to neutralisation. Another 100 c.c. are filtered, in like manner, into a strong quarter-litre flask, and diluted with about 100 c.c. of hot water; the requisite quantity of normal acid is then run in at once from a burette; the solution diluted to 250 c.c.; and about a gramme of dry barium carbonate (free from alkali) added. The flask is next closed and the liquid well agitated. The decomposition of the alkaline sulphate is completed in a few minutes. The flask should be opened now and then to allow the carbonic anhydride to escape. Finally, about ½ grm. of pulverised barium hydrate is added, the whole well shaken, and a portion of the rapidly clearing liquid tested qualitatively for barium and sulphuric acid. The result should be a negative one. 50 c.c. corresponding to 20 c.c. of the original solution are then filtered into a porcelain dish and standardized with normal acid (hydrochloric or sulphuric), and the quantity of sulphuric acid (sulphate) calculated as usual.

The source of carbonic anhydride is thus placed in the liquid itself, provided the quantity of potassic carbonate be not too small.

Atomic quantities of $K_2SO_4 + 2K_2CO_3 + 2HCl + BaCO_3$ when mixed with sufficient water, change into $BaSO_4 + 2KHCO_3 + 2KCl$, and it is therefore more than sufficient to add twice the quantity of potassium carbonate compared with the alkaline sulphate operated upon.

Barium hydrate is added with a view of removing any carbonic anhydride left in the liquid after boiling, which would otherwise dissolve some of the excess of baric carbonate contained in the precipitate.

Any barium hydrate not required to remove CO_2 is acted upon by the hydro-potassic carbonate, but does not influence the final result.

Phosphoric and oxalic acids the author proposes to remove by means of calcium chloride, chromic acid by deoxidising agents, such as alcohol and hydrochloric acid. Bohlig recommends this method for estimating sulphuric acid volumetrically in ashes, crude soda, Stassfurth salts, &c.

Solutions containing baryta are estimated in like manner by precipitation as carbonate, and decomposition with potassium sulphate in a solution containing free carbonic acid. Chlorine is determined volumetrically in solutions by first precipitating any metallic chloride with potassium carbonate added in moderate excess. The filtrate is made up to 250 c.c. and the excess of potassic carbonate determined in 50 c.c. by means of a normal solution of HCl. 125 c.c. of the solution are next treated with excess of silver oxide and made up to 250 c.c., well shaken (out of contact with the light) and filtered. 100 c.c. of the filtrate are standardized with normal hydrochloric acid solution. The difference between the quantity of acid required in the last experiment and that of the former experiment, multiplied by 5, gives the amount

of chlorine contained in the original solution. A portion of the filtrate should be tested for chlorine by means of mercurous nitrate.

The filtrate is obtained perfectly clear only in the presence of some potassic or sodic carbonate, and by employing argentic oxide free from argentous oxide. A few drops of pure potassium permanganate added to the argentic oxide preserved in water prevent the formation of the latter. The oxide to be employed for each experiment is filtered when required, and thoroughly washed.

Bromine and iodine are determined in like manner. The author has not been able, however, to estimate mixtures of the halogen salts; but he has made the interesting observation that potassium iodide, when boiled with potassium permanganate is completely oxidised into iodate. This facilitates the detection of small quantities of chlorine and bromine, in the presence of much iodide. The greater part of the iodate may be separated also by precipitation with baric nitrate before determining chlorine. The standard acid solutions which Bohlig employed contain not more than one-third of the equivalent of HCl or SO_3 per litre. The litre may be determined by means of pure potassium carbonate or ignited potassium sulphate.

The results given by the author are accurate.

W. V.

On Combustion Furnaces. By A. Müller.*

The author reviews several forms of combustion furnace, and claims special advantages for the following modification of Baumhauer's furnace:—The burner consists of an iron plate prismatic chamber, closed above by metal gauze of an appropriate mesh, and divided longitudinally into 10 chambers, each 80 millim. long; a gas-jet, furnished with numerous apertures, delivers gas into the middle of each chamber. The mixture of gas and air burns above the gauze under little or no pressure, and gives a flickering flame which readily deposits soot. To obviate this, iron-plate walls are arranged above the gauze to a height of 40—50 millim. To obviate the ill effects of expansion and contraction, the walls are cut up into short lengths, 2 for each chamber. The distance between the top edges of these walls is about 2 millim.

The tube to be heated is suspended over the burner, at about 20—30 millim. above the top of the walls, according to the degree of heat required. Over the tube are suspended, from a horizontal bar, a series of unglazed porcelain half cylinders, about 10 millim. thick, 40 millim. inside diameter, and 30 millim. long. The semi-cylinders are depressed so as to embrace about half the circumference of the combustion tube. The effect of this arrangement is to cause a reverbera-

* Deut. Chem. Ges. Ber., iv, 1.

tion of the flame upon the tube, with consequent equal heating of its upper and under sides. The flame is controlled longitudinally by iron or clay movable screens, which are laid in the required position on the top of the walls of the burner.

F. H. H.

Method for Water Analysis. Sulphuric Acid Estimation. By ALEXANDER MÜLLER.*

THIS method depends on the following facts:—Barium chloride completely precipitates sulphuric acid from *neutral* solutions, and barium is completely precipitated by *neutral* potassium chromate. If then a standard solution of barium chloride be added in excess to the solution of a sulphate, the whole of the latter is removed in the form of barium sulphate, and, on addition of a standard solution of potassium dichromate in excess (together with enough ammonia to neutralise it), the whole of the barium still in solution is precipitated in combination with an equivalent quantity of chromic acid. If the quantity of chromate solution employed were capable exactly of precipitating the barium chloride originally added, it is clear that the quantity of the former remaining in solution must be equivalent to the sulphate present in the liquid under examination.

The quantity of chromate so remaining can be estimated with accuracy by comparing the colour of the liquid acidulated by hydrochloric acid, with that of a standard solution of bichromate, in a suitable instrument. When a "water" is examined by this method, it is necessary to boil it well before adding the barium chloride, in order to prevent any precipitation of barium as carbonate. For other working details we must refer to the original paper.

C. H. G.

A Modification of Schlösing's Method of determining Nitric Acid. By E. REICHARDT.†

SCHLÖSING'S method,‡ as is well known, is based upon the evolution of N_2O_2 from a neutral or alkaline solution of a nitrate by means of ferrous chloride and hydrochloric acid and the collection of the gas over mercury. After removing any acid vapour by means of a little lime-water, the N_2O_2 is transferred to another vessel containing water, and excess of oxygen added, whereby it is again converted into nitric acid, to be determined finally by means of a very dilute standard solution of soda.

* Zeitschr. f. Chem. [2], vii, 55, from Deut. Chem. Ges. Ber., iii, 881.

† Arch. Pharm. xcv, 102; from Fresenius, Zeitschr. f. Analyt. Chemie.

‡ Fresenius, Quant. Anal. iv. Ed. p. 346.

Reichardt describes an apparatus for collecting the evolved nitric oxide gas over a solution of sodic hydrate (in which the gas is but very little soluble) instead of over mercury. The nitrate is heated in a small evolution flask, similar to the one employed by Schlösing, but fitted with a double-bored india-rubber cork, into which short bent glass tubes are inserted. Solutions of ferrous chloride and hydrochloric acid are successively sucked into the evolution flask, from which every trace of air has been previously displaced by brisk ebullition of the nitrate solution. This is done by opening and closing the Mohr's compression cock with which the glass tube is provided, care being taken to avoid sucking in any air. The other tube bent at a right angle is connected with a bottle fitted with a three-hole india-rubber cork. The tube nearest the evolution flask, also bent at a right angle, reaches nearly to the bottom of the bottle, as does likewise a tube leading to a second somewhat larger sized bottle, whilst a third short tube just passes through the cork, and is used for transferring the nitric oxide gas. These three tubes are all provided with india-rubber joints and Mohr's compression cocks.

The second bottle is fitted with a double-bored india-rubber cork, through which passes a glass tube, reaching nearly to the bottom and bent at right angles, by means of which it can be connected with the first bottle, also with a short upright tube provided with a small drying tube containing pieces of sodic hydrate. A weak soda solution is repeatedly sucked from the second to the first bottle, and driven back again by a current of pure hydrogen, till every trace of air has been displaced. Connection is then made with the evolution flask in such a manner as to exclude any air, by first filling the india-rubber joints with water. On connecting the evolution flask, charged as described, and heating it, at first gently, on a water-bath, and lastly over a gas flame, N_2O_2 is evolved, which is cautiously admitted into the first bottle, by opening the compression cock, a corresponding bulk of liquid being at the same time forced over into the second bottle. The operation is interrupted, when the gas-bubbles are entirely condensed by the liquid in the first bottle, by opening the tube through which the iron solution, &c., had been introduced into the evolution flask, and closing the tubes which connect the first bottle with the evolution flask and the second bottle.

The N_2O_2 is next transferred to a small flask charged with about 200 c.c. of water. The air is in like manner expelled by brisk ebullition of the water, and the gas sucked in by way of the short tube, fitted through the cork of the first bottle, and opening the connection tube between the first and second bottles. As it is essential that no alkali should enter the flask, the last traces of N_2O_2 have to be transferred from the first bottle by means of hydrogen gas, repeatedly

admitted to and expelled from the first bottle in the manner already described. Oxygen is then admitted to the flask, the gaseous mixture allowed to stand for about 25 minutes, and the amount of nitric acid formed determined lastly by a standard solution of soda.

By observing the necessary precautions, Reichardt obtained accurate results, and was able to perform a determination of nitric acid in less than half an hour. The contents of the two bottles are made to serve for repeated operations.

Reichardt* describes some comparative experiments on the delicacy of the sulphate of aniline and brucine reactions for nitric (nitrous) acid. He found that the aniline salt gave no more indications of the presence of nitric acid in a solution containing one part of nitre in 1,000 parts of water, while a solution of brucine gave distinct indications in solutions containing one part of nitre in 100,000 parts of water. To test a potable water qualitatively for nitric (nitrous) acid, Reichardt mixes a drop of the water with two to four drops of brucine solution—best in a porcelain dish—and then drops concentrated sulphuric acid (free from nitric acid) into it. In waters containing much nitric acid, the first drop of sulphuric acid usually gives a delicate reaction; if, however, as many as five drops of acid have to be added, he considers that little or no nitric acid is present in the water.

Reichardt† secures more perfect condensation of liquids of low boiling points, such as ether, &c., by interposing a narrow glass tube, bent doubly at right angles, between the condenser and the distilling flask. He also describes some movable holders for burettes, and a complete and cheap polariscope. W. V.

On the Estimation of Phosphoric Acid. By E. W. Parnell.‡

The author states that it is unnecessary to make the usual correction of ·001 grm. for every 54 c.c. of the filtrate and washings from the ammonio-magnesic phosphate precipitate, since the solubility of the precipitate in sal-ammoniac and ammonia is counteracted by the presence of excess of an ammoniacal solution of a magnesium salt, and, to a certain extent likewise, by that of a solution of sodium phosphate, and he infers, therefore, that the usual correction of ·001 grm. for every 54 c.c. is too high, when excess of sodium phosphate is present in the liquid. He found that from weighed quantities of pure magnesia, the theoretical quantity of the double phosphate could be obtained, without any correction for the filtrate, but he does not state what

* Fresenius, Zeitschr. f. anal. Chemie. ix, 2.

† Fresenius, Zeitschr. f. anal. Chemie. ix, 2.

‡ *Ibid.*, 145.

excess of the sodium phosphate had to be added, and to what extent the solubility of the precipitate was counteracted thereby.—[These observations are at variance with Fresenius's experiments].

W. V.

On the Estimation of Acetic Acid in Lead Acetate. By H. SEWARD.*

THE author dissolves the acetate in water (1 in 20), then adds litmus and a standard solution of sodium carbonate, and takes the change from a purplish neutral tint to a pale blue as indicating the end of the reaction.

W. V.

On the Analysis of Chrome Greens. By E. BOHLIG.†

THE author proposes to substitute potassium permanganate for the potassium chlorate and nitric acid recommended by Fresenius in the analysis of chromic oxide, according to the equation—

$$Cr_2O_3 + K_2Mn_2O_8 = K_2CrO_4CrO_3 + 2MnO_2.$$

He thus analysed Guignet's green, by first treating with hydrochloric acid then with potash, and finally digesting the residue in a porcelain dish with water, and adding permanganate solution from a burette, till the liquid just appeared permanently red from the excess of permanganate added.

W. V.

Determination of the Alkalies in Silicates by Ignition with Carbonate of Lime and Sal Ammoniac. By J. LAWRENCE SMITH.‡

IN 1853 the author published the results of a series of experiments upon the quantitative estimation of silicates, with the view of directing the attention of chemists to a new method which he had devised, in the first place, to facilitate the analytical decomposition of silicates, and, further, to obtain the alkalies in combination with hydrochloric acid, so that they may be weighed in the form of chlorides rather than in the form of sulphates.

Several years' practice having confirmed the results of earlier experience, it has been the aim of the author to embody in the present paper the process in its minutest detail, which process will be found quite distinct, both in operation and objects, from the method introduced by Deville by fusion with carbonate of lime.

The process consists essentially in the *ignition of the silicate with carbonate of lime and sal-ammoniac*, by which means, caustic lime dissolved

* Chem. News, xxiii, 102.
† Arch. Pharm. [2], cxlv, 126.
‡ Sill. Am. Journ. [3], i, 269.

in fused chloride of calcium is brought to act in a most thorough manner upon the silicate at a red heat.

About half a gram of the finely powdered silicate is intimately mixed with an equal quantity of sal-ammoniac, then four garms of pure precipitated carbonate of lime added, and the whole accurately mixed by trituration. It was found that when the above mixture was heated in an ordinary platinum crucible, a small quantity of the alkali was lost by volatilization; to eliminate this error, an improved form of crucible was adopted. The height of the crucible was increased to about $4\frac{1}{2}$ times the length of its diameter; length, 95 mm.; diameter of opening, 22 mm.; form, slightly conical; weight, about 40 grms. The mixture being introduced, the crucible is placed over a Bunsen burner in an inclined position, so that the heat is brought to bear just above the top of the mixture and gradually carried towards the lower part, until the sal-ammoniac is completely decomposed; the whole is then raised to bright redness, which is to be maintained for about 50 minutes. On cooling, the contents of the crucible will be found to be more or less agglomerated in the form of a semi-fused mass. The latter is then detached, if possible, placed in a beaker, and thoroughly disintegrated by boiling with distilled water. The alkalies originally contained in the mineral are now in solution as chlorides, together with a certain amount of calcium chloride, while the silica remains insoluble in combination with the excess of lime. Filter, precipitate the lime by the addition of carbonate of ammonia, heat the solution for a short time on a water-bath, add a few drops of caustic ammonia, and filter again to remove the precipitated carbonate of lime. The filtrate contains the alkaline chlorides and a little sal-ammoniac. Evaporate to dryness in a tared platinum dish, ignite gently, and weigh. The weight gives, as chlorides, the amount of alkalies contained in the mineral.

A special arrangement for heating the crucible by gas is described, but as this is by no means either necessary or important to the success of the operation, we omit further description concerning it.

The presence of boracic, hydrofluoric, and phosphoric acids in the silicate in no way interferes with the estimation; and the author prefers this method, even with silicates *soluble in acids*, on account of the ease and accuracy with which the analysis is performed.

J. W.

Detection of Morphine and Strychnine in presence of one another. By C. Neubauer.*

According to Otto, when a solution of the mixed salts of these alkaloids is rendered alkaline, and then shaken with ether, the

* Zeitschr. f. Chem. [2], vii, 64, from Z. Anal. Chem. 1870, 240.

strychnine dissolves, but not the morphine. Neubauer finds, however, that the first ethereal extract contains both alkaloïds, and the last extracts leave residues on evaporation, in which morphine alone can be detected. Amyl alcohol, however, always extracts more morphine from the ether-exhausted material.

C. H. G.

Estimation of the Value of Chloral Hydrate. By CARL MÜLLER.*

THE author has devised an instrument called a "chloralometer," which affords a ready method of estimating the amount of chloroform set free, when chloral hydrate is treated with caustic alkali, as in the usual process for determining its commercial value. He introduces into a graduated tube 25 grms. of the chloral hydrate to be operated on, adds somewhat more than the equivalent quantity of solution of caustic alkali, and closes the tube with a good cork. When the first violent action is over, the tube is carefully inclined and finally shaken, in order to complete the reaction. On standing two or three hours the chloroform completely separates; it can then be accurately measured, and the weight calculated from the known specific gravity at the observed temperature. Five trials with pure chloral hydrate gave 71·6 per cent., theory requiring 72·2 per cent. C. E. G.

Technical Chemistry.

On the Alleged Action of Cold in rendering Iron and Steel Brittle.†

REFERRING to the disastrous railway accident at Hatfield, on the Great Northern Railway, caused by the breaking of a steel tire, which was attributed to the intensity of the frost, Sir William Fairbairn‡ publishes a series of experiments on wrought-iron, made by him some years ago, which proved that the resistance of iron to a tensile strain was as great at the temperature of zero as it was at 60°, or upwards, until it attained a scarcely visible red heat; that, in fact, the mean breaking weight, in tons, per square inch, was in the ratio of 19·930 to 21·879, or as 1 : 1·098 in favour of the specimens broken at the temperature of zero. The generally received opinion is, however, against these facts, viz., that the strength of iron and steel is greatly reduced at the temperature below freezing. The contrary was proved to be the case in wrought-iron plates, and assuming that steel follows the same law, the cause for the fracture of the railway tire must, in the opinion of the author, be sought

* Zeitschr. f. Chem. [2], vii, 66—67.

† See page 167 of this volume.

‡ Proc. Lit. Phil. Soc. of Manchester, x, 86; Chem. News, xxiii, 89.

for, not so much in changes of temperature as in the practice of heating the tires to a dull red heat, and shrinking them on the rim of the wheels. Sir William proposes that the rim of the wheel and the inside of the tire should be turned to a standard gauge, accurately calculated, to give the required amount of tightness with a larger margin of strength.

J. P. Joule* seeks the cause of fracture of the tires of the wheels of railway carriages during cold weather, in the severer strain which is put upon the metal tires when travelling over frozen ground, and states that the theory of iron and steel becoming brittle at a low temperature is in defiance of all that is known of the properties of the materials, and of the experience of everyday life. Joule experimented with darning needles and garden nails, and applied tensile strain and falling weights, in order to test the resisting power at ordinary temperatures (55° F.) and at temperatures considerably below the freezing point (0° to 10° F.), and gives as the collective result of all, that the cold needles resisted better than the warm, and that equal numbers (21) of cold and warm nails broke; he thence concludes that frost does *not* render either iron (cast or wrought) or steel brittle.

In order to ascertain the effect of hardness upon the strength and elasticity of these small specimens of cast-iron, the author hardened them by first heating the nails nearly to the melting point and then plunging them into water. Those sufficiently hard to resist the action of the file were selected for the experiments; others he allowed to cool down slowly from a bright red heat. The average breaking weight was 125·2 for hardened nails, and 136·2 for soft nails; the average deflection was in the proportion of 0·0056 to 0·0080. By reducing these figures to the uniform dimensions of pieces of iron three feet in length and one inch square, making a deduction of one-sixth from the deflections, on account of the taper of the nails, they became—

	Breaking weight.	Deflection.
Nails in original state	2673	0·922
Hardened ,, ...	2002	0·677
Softened ,, ...	2448	0·924

R. Spence† has investigated the effect of cold upon cast-iron in regard to its powers of resisting transverse strain, either of weight or pressure, and finds that a specimen of cast-iron, having at 70° F. a given power of resistance to transverse strain, has that power increased by 3 per cent. at zero. The difference in the breaking weights actually required in the 140 different experiments, amounting to as much as 40 per cent., leaves it doubtful, however, whether a mean difference of only 3 per

* Proc. Lit. Phil. Soc. of Manchester, x, 917; Chem. News, xxiii, 101, 145.

† Proc. Lit. Phil. Soc. of Manchester, x, 94; Chem. News, xxiii, 109, 124.

cent., indicative of highly homogeneous iron bars, should be looked upon as conclusion.

W. V.

Chemical Phenomena of Iron Smelting. By I. L. BELL.*

THIS paper contains an account of Mr. Bell's preliminary researches on the conditions which determine the best size of the blast furnace and of the minimum temperature requisite for the chemical actions involved in iron smelting.

The author describes his experimental researches on the action of the different gases of the blast-furnace on iron and on oxide of iron at various temperatures. The bearing which these valuable experiments have on the questions of the best size of furnace and of the best temperature of the blast the author reserves for future consideration.

C. G.

The Chemistry of Iron Smelting. By C. SCHINZ. (Dingl. Polyt. J., cxlv, 117, 188, 273).

A Comparison between the Working of the Ordinary Puddling Furnace and the Siemens Regenerative Furnace. By Dr. KOSMANN.†

AFTER an examination into the construction and management of a Siemens' furnace and of the composition of the slags produced in an ordinary and in a Siemens' furnace, the author concludes that the Siemens' may be used with advantage :—

(1.) In processes which require great heat, or where cheap and otherwise useless fuel is to be had.

(2.) In all cases where a constant temperature and where a flame of a specific kind are required.

(3.) In circumstances where another motive force is available, such as water or waste steam power from other furnaces. In such cases a saving of 50 per cent. in fuel can be effected by the use of the Siemens'.

On the other hand, where cheap inferior fuel is not to be had, and where steam is not obtained as a waste product from other furnaces the employment of the Siemens' furnace is questionable.

C. G.

* Journ. Iron and Steel Inst., Feb., 1871.

† Chem. Centr., 118, from Grimmsberg u. h. Jahr. 6, xix, 341.

On Kröncke's Method of Amalgamating Silver Ores. By LOUIS EICH.*

THE author has submitted Kröncke's method, which is largely used on the western coast of South America for the treatment of the sulpho-arsenides and antimonides of silver, to a series of experiments in order to discover the chemical changes which take place in the process. The following are his results:—

(*a.*) On treating the finely-ground red ore with a hot solution of cuprous chloride and sodic chloride the powder becomes black. This powder on analysis proves to be composed of silver sulphide and cuprous sulphide, the solution containing antimonious chloride, thus—

$$3Ag_2S,Sb_2S_3 + 3Cu_2Cl_2 + NaCl = 3Ag_2S + 2SbCl_3 + 3Cu_2S + NaCl.$$

(*b.*) The silver sulphide acted upon by the same reagents in presence of zinc gives almost immediately a precipitate of metallic silver.

$$Ag_2S + Cu_2Cl_2 + Zn + NaCl = Ag_2 + Cu_2S + ZnCl_2 + NaCl.$$

The chief points to be attended to in working this process are:—

(1.) The employment of hot concentrated solutions of cuprous chloride and sodic chloride, the latter being necessary in order to obtain a greater quantity of cuprous chloride in solution and also to prevent the formation of basic copper salts.

(2.) The finely-ground ores must be used *dry*, in order that they may be rapidly and fully saturated with the solution, and also to avoid the formation of basic salts.

(3.) The amount of the amalgams of mercury with zinc or lead, and of the cuprous chloride, must be so regulated as to avoid the precipitation of the copper, which would then enter the amalgam and lead to difficulty. When this occurs, Kröncke treats the pressed amalgam with a hot solution of cupric chloride, obtaining the reaction—

$$CuCl_2 + Cu = Cu_2Cl_2.$$

C. G.

Improved process of Extracting Silver and Gold from Arsenio-Sulphides of Lead, Copper, &c. By C. WIDEMANN.†

THE author describes a process, recently patented by Cyprien Marie Tessié du Mothay, for the extraction of silver and gold from sulphurets, arsenio-sulphides and antimonio-sulphides of lead, copper, &c., containing the precious metals. The following are the main features of the process:—

* Chem. Centr., 1871, 121, from B. u., Hüttenm. Zeitung, xxx, 29.

† Chem. News, xxiii, 126.

1. The sulphur ores above mentioned are roasted with silicates, litharge being added to complete the oxidation.

2. The easily fusible scoria thus obtained is run on to a bath of molten lead with which it is thoroughly mixed by mechanical means. The molten lead is said to dissolve out the whole of the gold and silver. The scoria is then removed, and fresh charges of the fusible silicates are added until the lead becomes sufficiently rich for cupellation.

3. The siliceous scoria is reduced by charcoal and iron, and an alloy of lead and antimony obtained.

4. This alloy is freed from antimony by acting on it at a high temperature with steam, which oxidizes the antimony. The lead is freed from all traces of antimony by means of a small quantity of lead sulphate.

Should the alloy contain copper instead of antimony, lead sulphide is added, and the resulting scoria of copper sulphide is removed. The pure lead thus obtained is either sold or used in the treatment of fresh ore.

C. G.

A new Method for Refining Crude Silver. By F. Gutzkow.*

The well known method of obtaining refined silver by the separation of the gold, lead, copper, &c., through the agency of sulphuric acid and copper sulphate, has many important disadvantages. In the first place, the silver sulphate obtained in this process requires much water for its solution; inconveniently large apparatus must therefore be employed; and in the second place, a serious commercial difficulty arises from the fact that the refiner is obliged, in the cementation of the silver sulphate by metallic copper, to produce copper sulphate, which is already a product of so many technical operations, that its formation in the process necessarily leads to loss.

The author avoids these commercial difficulties by limiting the production of copper sulphate to the amount of copper contained in the raw silver bars. He has used the following method for many years in the works of the San Francisco Assaying and Refining Company. The hot thick liquid, obtained by treating the bars with sulphuric acid in iron vessels, is run into a large cast-iron pan containing sulphuric acid of 58° Baumé, heated to about 110° C. A small quantity of water is then added, and after a few minutes the now clear liquid is run off into a lower pan, surrounded with cold water. The amount of water added is regulated by the density of the acid solution; it not only serves to reduce the density of the acid liquid, containing the dissolved

* Deut. Chem. Ges. Ber., iv, 114.

metals to 58° Baumé, but also to precipitate the lead sulphate. The total amount of dilute acid employed is about 10 cubic feet for each centner of refined silver obtained. The heavy precipitate formed not only clarifies the liquid, but also carries down with it all gold that may be in suspension, a result of the highest importance, which renders this method of treating the liquids much superior to that of pouring the vitriol solution of the bars *into* water.

When the liquid in the lower pan has cooled down to 30° C. to 40° C., it is pumped off from the crystals of silver sulphate into an upper pan where it is again heated and used as acid. The silver sulphate thus freed from the mother-liquor is found as a hard yellow crystalline mass of from one to two inches thick, containing very little free acid. This is removed with iron shovels and placed in a leaden box on wheels having a false bottom from which the drainage-liquid can be run off.

Mixed with the crystals is found a red powder, consisting essentially of copper sulphate. A hot concentrated solution of ferrous sulphate is then run through the mass; the copper sulphate is first dissolved and the first portion of the filtrate is collected in a separate vessel in order afterwards to obtain the blue vitriol from it. When the filtrate shows the pure brown colour of the ferric sulphate, it is collected in a shallow pan in order that the dissolved silver sulphate, and with it the metallic silver, may be precipitated on cooling. This powder is afterwards added to the main mass in the filter. The crystals in the filter are gradually converted into a coherent mass of metallic silver, and the operation is judged to be finished when the filtrate shows the pure green colour of ferrous sulphate. The metallic mass is then thoroughly washed with pure water, pressed by a hydraulic machine, and melted.

The oxidized iron solution, after being cooled, is treated with scraps of iron, in order to reproduce ferrous sulphate for fresh operations. The small quantity of copper and silver which is here precipitated by the iron, is placed from time to time in the silver sulphate filter in which the copper is soon dissolved.

The amount of concentrated ferrous sulphate used is about 20 cubic feet (German) for every centner of reduced silver obtained in the filter.

C. G.

On the Roasting of Sulphur Ores, with a Description of a New Roasting Oven. HASENCLEVER and HELBIG. (Dingl. Polyt. J., clxv, 284.)

Experiments on the Utilization of the Residue obtained from Roasting Iron Pyrites. C. RECHTERS. (Dingl. Polyt. J., cxlv, 292.)

Silvering and Gilding of Silk. By WITHELM GRÜNE.*

THE silk is soaked with a 5 per cent. solution of iodide of potassium, and dried, then (in non-actinic light) dipped in a 5 per cent. solution of nitrate of silver containing a few drops of nitric acid, and well drained; next exposed for a few minutes to sunlight, and then dipped in a 2 per cent. solution of sulphate of iron. It immediately becomes grey from reduction of metallic silver, and after washing and drying, only requires burnishing in order to acquire the metallic lustre. By repeating this treatment, varied, however, by adding a little free iodine to the solution of iodide of potassium, the silver deposit becomes stronger. By laying the silvered silk in a very weak solution of chloride of gold, the silver becomes chloride, and gold is deposited; and by then removing the chloride of silver with a solution of hyposulphite of soda, washing, drying, and burnishing, the appearance of gilding is produced if the deposit of metal be sufficiently stout. It is quite necessary to use pure chemicals.

C. H. G.

A Comparative Pyrometric Valuation of Kaolins. By C. BISCHOFF.†

THE author describes the results of his experiments on different specimens of kaolins, in order to determine their fire-proof values. This method consists in heating small cylinders of the clay to the melting-point of platinum. This is repeated; the cylinder is then weighed, crushed, and mixed with the author's test-substance, consisting of 2 parts of pure alumina and 1 part of pure silica. This test-substance is added in proportions of $\frac{1}{10}$ of the weight of the cylinder, the cylinder being heated to the melting-point of platinum after each addition. This is repeated until the cylinder remains unglazed and the structure becomes granulated. The value of the kaolin is estimated by the quantity of the test-material required. This varies from $\frac{2}{10}$ to $\frac{10}{10}$ of the weight of the cylinder.

In a postscript the author gives the results of his experiments to determine the comparative action of ferric oxide, lime, magnesia, and potash in rendering silica fusible. He found that, in order to render 100 parts of silica fusible at the melting-point of platinum, the following amounts were needed:—

F_2O_3	100 parts, or equal weights.
MgO	45—50.
CaO	40—45.
K_2O	20—30.

C. G.

* Chem. Centr., 1871, 174.

† Dingl Polyt. Jour., cxcviii, 396—411.

On the supposed Incapability of Potash to form Ultramarine. By W. STEIN.*

IN examining this question, the author prepared a "frit" from Meissen clay (Meissner Thon) and 1·4 part carbonate of potash. This was milk-white, and in outward appearance resembled the usual soda "frit," so that probably its optical properties would not interfere with the production of a blue colour. He then proved that sulphide of potassium is capable of forming sulphide of aluminium when fused with alumina. Next, that when potash frit and soda frit are exposed side by side to the vapour of sulphide of carbon at a red heat, similar black masses are formed, both containing the essential (for the formation of ultramarine†) black sulphide of aluminium. When these sulphuretted frits were washed with water, that containing soda remained unaltered, but that with potash softened and evolved abundance of sulphuretted hydrogen, losing at the same time its colour and becoming dirty green. This difference is to be ascribed to the greater ease with which potassio-aluminic silicate is attacked by water as compared with the corresponding soda compound. If the silicate which encloses the particle of aluminic sulphide is decomposed or dissolved, the latter comes in contact with water and is destroyed; therefore if potash ultramarine is formed it will be destroyed by water.

C. H. G.

On the Colouring of Cemented Work. By H. FRÜHLING.‡

THE addition of colouring matters to cement more or less injures its setting power, and fails to produce pure tints. Cheap and permanent colour-washes may be made by mixing equal volumes of the dry pigment and burned and washed flint with milk of lime; a little water-glass may be advantageously added. The tint produced is very agreeable, and, if stable mineral colours be used, as durable as the cement itself.

Surfaces of great beauty are produced by finely powdered marble and flint, with the faintest tint of chrome-green. The wash should be applied as soon as possible after the cement has set, and if possible in one coat only; but if two are necessary, the second must be made with the addition of water-glass. It is indispensable that the work be freely wetted for a week after laying on the colour.

F. H. H.

* J. pr. Chem. [2], iii, 137.

† See p. 167 of this volume.

‡ Dingl. Polyt. Journ., cxcix, 497.

Amorphous Silicic Acid as Mordant for Colouring Matters. By M. REIMAN.*

PRECIPITATED silicic acid possesses enormous power of absorbing colouring matters from solution, especially the aniline colours. The hydrated silica coloured with fuchsine, aniline blue, or aniline violet, retains these colours when washed with cold water, but partially gives them up when boiled with water or spirit. The coloured powders obtained are brilliant, and adapted for calico printing. By help of hydrated silica it is easy to fix, even on cotton, those colours which will not dye in a direct manner. For this purpose it is only necessary to pass the cotton through a solution of water-glass, then through dilute acid, and to thoroughly wash, in order to give it the power of absorbing the aniline colours with production of fresh and lively tints, which more nearly approach the colour of the original dye-stuff than do those produced on cotton mordanted with tannin.

The action of the silica is a surface action, and is not due to the presence of traces of alkali, as is proved by the fact that glass, the surface of which has been etched by hydrofluoric acid, possesses the same power of taking up those colours.

C. H. G.

Bailey's new Bleaching Process with Sulphurous Acid. By FR. FRESENIUS.†

THE well-washed material is introduced into a turbine, which is then closed by a cover having a communication with an apparatus in which sulphur can be burnt. On setting the turbine in motion, air containing sulphurous acid is drawn into the apparatus to replace that expelled by the centrifugal force. The moist material absorbs the acid gas. The turbine is not seriously attacked by the sulphurous acid if it be occasionally washed out with a weak alkaline solution.

C. H. G.

On the Reactions of various Oils with Sulphuric Acid. By G. P. CLARKE.‡

OILS were experimented upon which were as far as possible perfectly pure. Their sp. gr. was determined at 15° C. The proportion of acid to oil was as 1 to 25. Each experiment lasted ten minutes, and the changes produced by the acid were observed carefully with a large magnifying glass. For the details we must refer to the paper itself.

W. V.

* Chem. Centr., 1871, 61.
† Chem. Centr., 1871, 174.
‡ Chem. News, xxiii, 145.

On the Physical Properties and the Heating Power of different Petroleums from Russia. By H. SAINTE-CLAIRE DEVILLE.*

THE oils which the author examined came from Baku, on the Caspian Sea, and were sent to him for the determination of their commercial value.

Petroleum is chiefly used for burning in lamps. A good lamp-oil must be fluid enough to be taken easily up by the wick, and at the same time not too volatile; these two conditions are fulfilled by that portion which boils between 150°—300°; that boiling below this temperature is too volatile, giving rise to dangerous explosions; whilst that boiling above 300° is too viscid, and can be only used as lubricating oil or as fuel.

On subjecting the different samples to fractional distillation, the following results were obtained:—

1. Crude Naphtha from the Balchany Wells.	2. Residue from the stills at the Baku Works.	3. Black oil from Weyser's works in Baku.
Matter volatile below—	Matter volatile below—	Matter volatile below—
100° .... 1 per cent.	240° .. 1 per cent.	200° .. 2·3 per cent.
160° .... 5 ,,	260° .. 2·3 ,,	240° .. 8 ,,
180° .... 9·3 ,,	280° .. 4·3 ,,	260° .. 14 ,,
200° .... 14 ,,	300° .. 7·7 ,,	280° .. 22·3 ,,
220° .... 15·3 ,,		300° .. 33·7 ,,
260° .... 29 ,,		
280° .... 37 ,,		
300° .... 41·3 ,,		

It is thus seen that Nos. 1 and 3 will yield a certain quantity of lamp-oils, and that No. 2 can only be used either as lubricating oil or as fuel.

The following two samples, which the author had obtained in large quantities, were used to determine the heating power of these oils:—

4. Light oil.	5. Viscid oil.
Matter volatile below 140° .. 2·7 p. c.	Matter volatile below 200° .. 1 p. c.
,, ,, 160° .. 7 ,,	,, ,, 220° .. 1·3 ,,
,, ,, 180° .. 13·3 ,,	,, ,, 240° .. 1·7 ,,
,, ,, 220° .. 19 ,,	,, ,, 260° .. 3 ,,
,, ,, 240° .. 23·3 ,,	,, ,, 280° .. 6 ,,
,, ,, 260° .. 29·3 ,,	,, ,, 300° .. 9·7 ,,
,, ,, 285° .. 36·7 ,,	
,, ,, 300° .. 73·3 ,,	

* Comptes Rendus, lxxii, 191.

The author had already, on a former occasion, pointed out that petroleum expands very much by heat, and that, therefore, in order to avoid dangerous explosions, the barrels ought never to be completely filled, if they are subjected to a great variation of temperature. He has determined the specific gravity of the different samples at 0° and 50°, and calculated the coefficient of expansion—

	Specific gravity.		Coefficient of expansion.
	At 0°.	At 50°.	
No. 1	0·882	0·8473	0·000817*
„ 2	0·928	0·888	0·00091
„ 3	0·897	0·865	0·000737
„ 4	0·884	0·854	0·000724
„ 5	0·938	0·907	0·000681

If now, to be on the safe side, we assume that the temperature may vary within 50° during the transport, we can easily find how much space ought to be left empty in each barrel by multiplying its capacity with 50 × coeff. of expansion.

To find the theoretical heating power, the author determined the composition of the different oils—

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Hydrogen	12·5	11·7	12·0	13·6	12·3
Carbon	87·4	87·1	86·5	86·3	86·6
Oxygen	0·1	1·2	1·5	0·1	1·1
	100·0	100·0	100·0	100·0	100·0

To calculate the heat of combustion from these numbers, we must subtract from the hydrogen $\frac{1}{8}$th of the oxygen, multiply the difference by 344·62, and add to the product the quantity of carbon multiplied by 80·8.

Theoretical Heat of Combustion:—

No. 1	11370 cal.
„ 2	11000 „
„ 3	11060 „
„ 4	11660 „
„ 5	11200 „

* The coefficient of expansion of the light American petroleum is, according to my determinations, about 0·0008 at temperatures below 50°.—C. S.

These numbers are higher than those found by experiment, as by the combination of carbon with hydrogen a certain amount of heat is given out, but, as Macquorn Rankine has very justly remarked, the numbers are quite near enough to allow a comparison of the value of mineral oils as fuels.

By previous experiments, the author found that the heavy coal-tar oil has nearly always the same composition, and that it gives with a really remarkable regularity always the same quantity of heat when burned in a properly constructed calorimeter. Its sp. gr. at 0° is 1·044; one kilogram gives, on burning, 8916 heat-units, and yields 12·77 kilo. of steam. This oil the author uses as a standard to compare the actual heat of combustion of his samples.

He employed as calorimeter a steam-engine of 8 horse-power, which was provided with a Belleville boiler, in which, during the experiment, the pressure was kept constant within $\frac{1}{10}$th of one atmosphere. By means of this engine, air was pumped into an iron reservoir of 40 cubic metres capacity, provided with a stopcock, through which the air escaped under a constant pressure of $2\frac{3}{4}$ atmospheres.

The following numbers were obtained :—

	Pressure of steam in atmosphere.	Pressure of air in reservoir in atmosphere.	Temperature of feed-water.	Water volatilized.	Oil consumed.
Standard oil ..	3·8	2·65	26°	161 kilos.	18·23 kilos.
Oil No. 4	3·8	2·75	26·2°	175 „	15·45 „

From the numbers in the last line we obtain the number 11460 heat units. One kilo. of oil No. 4 produces under the ordinary pressure, and without work being done, 16·4 kilo. of steam. Oil No. 5 gave 126·6 kilo. of water volatilised for 11·852 kilo. of oil consumed—hence the heating power is 10800 heat units.

1 kilo. produces without work, and under the ordinary pressure, 15·55 kilo. of steam. On comparing these numbers with those calculated from the composition, we find—

	Found.	Calculated.	Difference.
No. 4	11460	11660	200
„ 5	10800	11200	400

We have thus a mean of difference of 300 heat-units, and if we assume that the other samples give the same difference, we come to the following results :—

	Found.	Calculated.
No. 1.....	11070	11370
„ 2.....	10700	11000
„ 3.....	10760	11060

The heating powers of those Baku oils are higher than those of the petroleums of America and Europe, which the author has previously examined.

C. S.

On the Part played by the Salts and uncrystallisable Sugar in the Generation of Molasses. By E. FELTZ.*

THE author has attacked this much disputed question, by experiments carried out in a form analogous to the conditions obtaining in actual work, *i. e.*, he "boiled" various artificially prepared syrups in a partial vacuum. For this purpose a two-necked flask was employed, one neck of which carried a thermometer and a bent tube for introducing the syrup, and the other, a tube leading to a condenser delivering into a graduated tube, in which the water distilled off could be measured. This measuring tube was put in connection with the vacuum of the factory.

In all the experiments a syrup containing 50 per cent. of sugar was employed, and to this was made the required addition of salt, &c. The first experiments were made with syrup, to which, salt, saltpetre, or a mixture of both, or lastly salt, saltpetre and uncrystallisable sugar had been added. They gave as a result: that the sugar retained in the molasses did not exist as a compound with a chloride or as a solution in uncrystallisable sugar. The explanation of the formation of molasses is to be sought in the physical nature of molasses itself. The characteristic viscosity was produced only in the last of the above named experiments, viz., where uncrystallisable sugar had been added—this not only hindered the crystallisation, but also the concentration.

Experiments made on the behaviour of mixtures of the two sorts of sugar alone, showed that even large quantities of uncrystallisable sugar would not prevent the crystallisation of that portion of the cane-sugar which was in excess as compared with the water remaining in the mass; but that the evaporation was rendered difficult, and the ultimate crystallisation very slow. When the two sugars were present in about equal quantities, concentration could not be pushed far enough to reduce the water below the amount which could retain all the cane-sugar in solution.

From these observations the author concludes that uncrystallisable substances, whether invert sugar or those classed as organic non-saccharine bodies, are the true molasses builders, and that they act as such in two ways: 1st., by preventing a sufficient degree of concentra-

* Chem. Centr., 1871, 165, from J. des Fabricants de Sucre, 1870, 52.

tion; and, 2ndly, by rendering a boiled mass so sticky, that even if sugar-crystals are formed, they cannot be separated from the syrup.

C. H. G.

On the Influence of Certain Organic and Inorganic Salts on the Crystallising Power of Cane Sugar. By A. MARSCHALL.*

As to the nature of the bodies which retain sugar, and prevent its fully crystallising from solution (the so-called molasses makers), nothing certain has yet been made out. Generally, the salts contained in sugar juices are considered as the principal cause of the formation of molasses, and the author set himself the task of determining in what degree the various salts possess this power. He enclosed sugar in tubes, together with a quantity of a solution of various salts, such as occur in beet-juice, the water of which was less than half the weight of the sugar, and therefore incapable of dissolving the whole of the latter at ordinary temperatures. The tubes were sealed and warmed till all the sugar was in solution, and then allowed to remain at rest in a cool place for 17—21 days; sugar crystallised out. The tubes were opened and the mother-liquid examined, by estimating the sugar, water, and salt contained in it. If the given salt had the power of preventing the crystallisation of sugar, the mother-liquid obtained should contain a proportion of sugar to water greater than 2 : 1 which is that which obtains in pure aqueous saturated solutions. In this way he obtained results which led to classifying salts, as—1st. Negative molasses makers; 2nd. Indifferent bodies; and 3rd. Positive molasses makers.

The negative molasses makers, or bodies which diminish the solvent power of water for sugar are—sodic sulphate, nitrate, acetate, butyrate, valerate, and malate; magnesic sulphate, nitrate, and chloride; and calcic chloride and nitrate.

The indifferent bodies which are without influence on the crystallisation of sugar are—potassic sulphate, nitrate, chloride, valerate oxalate, and malate; sodic chloride, carbonate oxalate, and citrate; and caustic lime.

Positive molasses makers are—potassic carbonate (saline coefficient 3·8), acetate (saline coefficient 0·9), butyrate (saline coefficient 0·9), and citrate (saline coefficient = 0·6). Betaine was shown to be a negative molasses maker.

C. H. G.

* Zeitschr. f. Chem. [2], vii, 63, from Zeitschr. d. Ver. f. Rübenzucker Industrie, 1870, 339.

On the Manufacture of Starch Syrup and Starch Sugar. By CARL KRATKE.*

THE author finds that the addition of 2 oz. (4 "loth") of concentrated nitric acid for every pound of sulphuric acid employed in converting starch into sugar, diminishes the time of boiling by one-half.

The paper contains useful working details, but says nothing about any action of the nitric acid on the copper steam worm.

C. H. G.

The Centrifugallising of Raw Sugar. By Dr. OTTOKAR CECH.†

THE author mentions that, in certain Bohemian sugar factories, it is found more advantageous to turbine the mass coming from the vacuum pan, than to allow it to drain in moulds.

C. H. G.

Researches on Malting without Germination. By H. FLECK.‡

THE author does not consider that he has come to a definite conclusion, or that his results can as yet be applied on a large scale. The substance of his paper is that barley, when steeped in a warm 1 per cent. solution of sulphuric, hydrochloric, or nitric acid for 72 hours, undergoes the same chemical changes as when allowed to germinate. He finds that nitric acid gives the best results, inasmuch as the "artificial malt" thereby prepared keeps better, and has all the odour of true malt.

Experiments on a small scale showed a yield of 92 to 94 per cent. of good kiln malt. Nothing is said as to the fermentability of the wort from such malt.

C. H. G.

Aëration of Must. By C. WEIGELT.§

THE results hitherto obtained by the use of von Babo's apparatus for aërating must (the must-whisk) show that wine made from must thus aërated always comes to maturity sooner than the wine made from the same must, but without the use of the must-whisk. Sometimes the quality of the wine is also improved. This earlier maturity of the wine, by allowing its early sale, is in itself a great advantage. Experiments undertaken by the author tend to show that this effect of the air is due to a precipitation of albuminous matters, and he thinks it possible that this precipitate consists of vegetable fibrin. The

* Polyt. C. Bl., xxiv, 1689.
† Dingl. Polyt. Journ., cxcviii, 428.
‡ Dingl. Polyt. J., cxlix, 145.
§ Chem. Centr., 1871, 58—66.

union of the vegetable paraglobulin and fibrinogenic substance contained in the must is, under ordinary circumstances, retarded by the sugar (sugar also retards the coagulation of blood), and when fermentation has once begun, the paraglobulin is precipitated by the carbonic acid produced, and of course no fibrin can be formed. Air, however, induces the combination of these two substances, in spite of the presence of sugar, and hence the precipitation of vegetable fibrin.

A. D.

Food Supplies of Paris during the late Siege.

THE following papers, referring chiefly to the artificial food supplies of the French capital during the late siege, possess some scientific interest.

Method of Purifying Fats. By A. BOILLOT. (Compt. rend., lxxi, p. 36).—One kilo. of the fat or suet to be purified is mixed with two litres of lime-water, and the whole is agitated for two or three hours, keeping the mixture heated. This is then cooled, and when the fat becomes pasty it is decanted and submitted to pressure in linen or flannel bags. Some water and oleic acids, containing still some solid fatty acids, flows away, and can afterwards be readily freed from these latter. The oily substance, after two or three days' repose, becomes of a desirable whiteness, and can be used for illuminating purposes after the small quantity of lime it contains has been removed by dilute sulphuric acid. Suet thus prepared loses its bad odour, and has acquired remarkable hardness and whiteness. After being melted beneath acidulated water, it forms a product well fitted for an illuminant, and for all the uses to which the best fats are applied.

Note on Suet and the Alimentary Fats. By M. DUBRUNFAUT. (*ibid.*, p. 37).—The most tainted suet is deprived of its characteristic odour when it has been fried, and after appropriate frying it may be used for any culinary operation, even the making of pastry. These facts are susceptible of a satisfactory scientific explanation.

The author has ascertained that fish-oils are entirely deprived of their odorous principle by simply heating them to a temperature of 330°, and he has also demonstrated that the fatty acids distil over with steam at a temperature above 100°, whilst the neutral fats are fixed under the same conditions; further, that the neutral fats behave like the fatty acids when submitted to a current of steam at a temperature of 300°—330°. Cooks, who do not use thermometers, have various empirical methods for ascertaining temperatures. One of these is the appearance of a white vapour which fatty bodies emit at high temperatures. The maximum temperature for good fryings does not exceed 210°—220°, when the substances are cooked in the minimum of time, and

absorb the minimum of fatty matter. Fricassees at 150°—160° are frequently made, and absorb the maximum of fatty bodies.

Under these conditions, all the circumstances most favourable to the elimination of volatile fatty acids are met with. All the fats sold for consumption are more or less odorous,but are yet less odorous than the unprepared fats; and the latter are more easily depurated than the former. In order to practise this depuration in the kitchen, it is simply necessary to raise the fat to a temperature of 140°—150° in a frying-pan, and then cautiously sprinkle upon it small quantities of water. The steam thus evolved carries off with it the neutral offensive fatty matters thus decomposed, and volatile fatty acids. This method of purification is capable of receiving numberless modifications, according to the particular substance to be prepared.

In a further communication (*ibid.*, p. 57), Dubrunfaut states that the conditions for effective depuration exist in a high degree in the process of roasting meat, and in a still higher degree in the preparation of the French *pot-au-feu*. He has also purified by a similar method colza oil, so as to deprive it of all unpleasant taste and smell, and he thinks that colza oil thus prepared may be usefully employed in alimentation.

A. Wurtz and E. Willm have found that colza oil, when submitted to a current of steam heated to 116°—120°, loses its odorous principle and acidity without becoming saponified to a sensible extent. After this treatment, it furnishes, when washed with a warm dilute solution of sodic carbonate, to remove all fatty acids, a substance capable of many useful applications.

On the Purification of Fats and Suets from Slaughter-houses for Use as Food. By Ch. Fua (*ibid.*, p. 59).—The author recommends the process of Dubrunfaut, described above, for purifying fats by depriving them by heat of their cellular tissue, and states that it is inexpedient to add any foreign matters during the depurative process. He recommends simple boiling of the fatty matters for some time over the fire.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XVIII.—*A new Double Salt of Thallium.*

By R. J. Friswell.

The platino-cyanides are well known for their tendency to form double salts, and I have now to lay before the Chemical Society some experimental results which show that this tendency is capable of development in a direction not hitherto contemplated.

Sometime since I wished to prepare some specimens of the platino-cyanides; amongst others, that of thallium. I could find no description of the method of preparation, and so had to discover a suitable process.

It occurred to me that the necessary reaction might take place between thallious carbonate CO_3Tl_2, and potassic platino-cyanide, and I accordingly mixed a small quantity of the solutions of the two salts. The solutions were both very hot, as thallious carbonate is but slightly soluble in cold water, and a hot solution begins to deposit it if only slightly chilled.

The mixed solutions were left to cool slowly in a covered beaker, and after a short time, while the solution was yet very warm, masses and tufts of splendid bronze green dichroic crystals began to grow from the sides and bottom of the beaker, and from the surface of the solution. These I collected with as little injury as possible, by detaching them by gentle shaking, and then pouring the whole on to a filter. The mother-liquor was removed by a slight washing with perfectly cold distilled water, in which the crystals proved almost insoluble. (In subsequent preparations I found it desirable to omit this as it spoiled the lustre of the crystals.) The crystals were dried at 100° in a water-oven, and were found to be of a magnificent crimson red by transmitted light, while the reflected colour was an intense bronzy green of strong metallic lustre. So vivid is this latter colour by daylight, that a friend to whom I exhibited them took them for brass filings.

I at first thought that this salt was the platino-cyanide I wanted, but soon found that this was not the case, as it effervesced strongly when treated with acids, evolving a quantity of carbonic anhydride, the effervescence continuing for a considerable time and a pale pink residue being left. I found that the platino-cyanide of thallium was yellowish white and completely destitute of dichroic tints, and that it could be prepared by decomposing baric platino-cyanide with an

equivalent quantity of thallious sulphate, filtering off the baric sulphate formed, and crystallising. It being evident that the salt I had obtained was not the platino-cyanide of thallium, I proceeded to make analyses.

0·2991 grm. was burnt with granular oxide of copper in vacuo, and the gases passed over ignited metallic copper, the vacuum being produced by means of a Sprengel pump, as described by Frankland and Armstrong in their paper on water analysis.* The gases were pumped off and analysed; they gave 5·089 per cent. of carbon, and 4·697 N. Repeated determinations of the nitrogen gave 4·607, 4·679, and 4·586. The carbon came out rather higher, the mean of five experiments giving 5·204.

The thallium was estimated as thallious iodide (TlI), by precipitating with potassic iodide in a solution made alkaline with ammonia, which renders the iodide very insoluble.

0·3452 grm. gave 0·3890 thallious iodide, equivalent to 0·2395 thallium or 69·37 per cent. 0·4965 grm. gave 0·5596 TlI, equal to 0·3448 Tl, or 69·24 per cent. Mean 69·305 per cent.

The platinum was estimated by fusing the salt with potassic disulphate, which converted the thallium into thallious sulphate, decomposed and liberated the cyanogen and carbonic anhydride, and left the platinum in the metallic state.

0·2635 grm. gave 0·0446 grm. Pt, or 16·88 per cent.

These results suggest that the salt is a compound of 1 molecule of thallious carbonate with 1 molecule of thallious platinocyanide, or $PtTl_2Cy_4,CO_3Tl_2$; the molecular weight of this compound is 1177·4, and theory requires the following percentage composition:—

		Found (average).	
C_5	5·10	5·20	
N_4	4·76	4·66	
O_3	4·08	3·96	by loss.
Pt.....	16·76	16·88	
Tl_4.....	69·30	69·30	
	100·00	100·00	Tl = 204·0 Pt = 197·4

The salt, when treated with warm nitric acid, effervesced evolved carbonic anydride, and left a pink residue. This was well washed with warm water and boiled, when it dissolved, and on cooling, crystallised out in long colourless needles. These were burnt as before. 0·3242 gave 6·785 per cent. carbon and 7·916 nitrogen, results corresponding to thallious platino-cyanide, which contains 6·76 per cent. carbon and 7·86 nitrogen.

The salt may be prepared by mixing 4·334 grms. of $PtK_2Cy_4,3OH_2$

* Journal of the Chemical Society [2], vi, page 90.

with 9·360 grms. of thallious carbonate, when the following reaction takes place :—

$$\mathbf{Pt}K_2Cy_4 + 2\ \mathbf{C}OTlo_2 = \mathbf{Pt}Tl_2Cy_4\ \mathbf{C}OTlo_2 + \mathbf{C}OKo_2.$$

When the salt is treated with potassic iodide, it is decomposed as follows :—

$$\mathbf{Pt}Tl_2Cy_4\mathbf{C}OTlo_2 + 4KI = 4TlI + \mathbf{Pt}K_2Cy_4 + \mathbf{C}OKo_2.$$

It may also be prepared by mixing 7·094 grms. of thallious platino-cyanide with 4·680 grms. of thallious carbonate when simple combination takes place.

Also by mixing 4·384 of baric platino-cyanide with 9·360 of thallious carbonate, when the reaction occurs as follows :—

$$\mathbf{Pt}BaCy_4 + 2\ \mathbf{C}OTlo_2 = \mathbf{Pt}Tl_2Cy_4\mathbf{C}OTlo_2 + \mathbf{C}OBao''.$$

The formation from potassic platino-cyanide is very curious, and is also a delicate reaction, as a crystal of thallious carbonate is at once stained red if moistened with solution of potassic platino-cyanide.

The salt is nearly insoluble in cold water, and is dissolved with difficulty by hot. The aqueous solution is absolutely colourless, and, unless very concentrated, does not deposit the salt on cooling. It, however, deposits white crystals, which are either a hydrate, or merely a mixture of the two constituents deposited simultaneously, but I have not yet determined which, though I am strongly inclined to the latter view.

To recrystallise the salt, it is best to use a hot aqueous solution of thallious carbonate, made so dilute that it does not deposit on cooling. I have examined the aqueous solution with the spectroscope, but have found no absorption bands, though, from the deep colour of the crystals, I expected to do so.

The crystals under the microscope appear to be hexagonal prisms, terminated by planes at right angles to the longer axis. Some crystals I have observed with splinters broken off from them longitudinally, somewhat in the way that a glass rod will break if struck on the end. The fracture in this direction is conchoïdal, and shows no signs of cleavage planes.

What the crystalline form really is, I am unable to say. But if, as I presume, is generally admitted, the formation of a true double salt depends upon the isomorphism of its constituent salts, and the resultant is isomorphous itself with those constituents, then this platino-cyano carbonate of thallium must belong to the trimetric system, to which thallious carbonate belongs,* as does also thallious platino-cyanide.

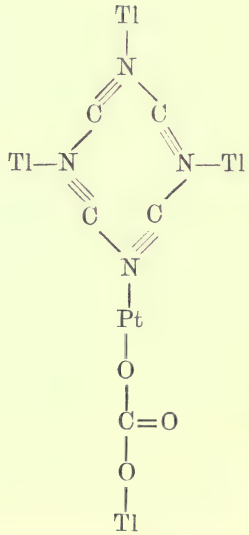
I use the term true double salt above, in reference to this compound, advisedly, and mean thereby an actual molecular combination, and not a body of a more complicated nature, such as an alum.

* Watts's Dictionary of Chemistry, vol. v., page 753.

My best thanks are due to Mr. J. J. Day, for the kind assistance he has rendered me in performing the combustions of the salt.

Discussion.

The President thought the communication just read was an important contribution to the knowledge of the double cyanides. It appears that the compound is formed only at the moment of solidification; it is an interesting phenomenon to see the beautifully coloured crystals shooting out from the colourless mother-liquor. With regard to Mr. Friswell's view that the new salt is a *molecular* combination of thallious carbonate and thallious platinio cyanide, the President was inclined to dispute this. If it is to be considered as a molecular compound at all, then it must be a triple, not a double, salt, for certainly there are three molecules in it, viz., thallious cyanide, platinous cyanide, and thallious carbonate. Now, such a definitely crystalline body may with greater probability be regarded as an *atomic* compound, the platinum affording the link between the thallious cyanide and the thallious carbonate, thus:—



Such a representation would also make the formation of the salt appear very simple. The idea of viewing the double cyanides as atomic compounds ought to receive more attention than chemists hitherto have given to it. These cyanides are much too stable to be regarded as mere loose molecular combinations.

Professor Williamson thought that most chemists are in the habit of considering the double cyanides as atomic compounds; there is hardly any alternative but to look upon so great a number of atoms as bound together by atomic forces. As to the particular mode of representation, however he had some hesitation in exactly following it.

Mr. Spiller inquired whether the thallium was disguised in the salt, or whether it gave the usual reactions, and if the latter was the case, whether *all* the thallium could be precipitated?

Mr. Friswell replied that the metal gave all the known reactions, and that potassic iodide and hydrochloric acid precipitate the whole of it.

Mr. Perkin inquired whether the pink colour of the residue that was left on treating the new salt with an acid may not be due to an admixture of some undecomposed salt?

Mr. Friswell replied that it was not.

The President asked Dr. Gladstone whether physical observation could not throw some light on the formation of these crystals from a colourless liquid.

Dr. Gladstone thought that this new double cyanide would be an interesting material to investigate. From the change of colour of the crystals from the colourless liquid he would assume that a molecular change had taken place.

The President suggested that an examination of the isomeric cyanides where the nitrogen is trivalent in one case, and quinquivalent in the other, should reveal differences in the refractive powers.

Dr. Gladstone said that he had determined the refractive indices of several isomeric bodies and found them to be different. The nitrous element in such bodies has a greater power of retarding the motion of light than it has in ordinary nitrates, for instance potassic nitrate.

Dr. Müller and Dr. Mills observed that there are many cases known where colourless solutions deposit coloured crystals, such as mercuric iodide, the double cyanide of lead and platinum, &c.

Note.—Since writing the above, a further examination of the salt has induced me to modify my views with regard to its constitution, and to incline to those expressed by the President in the discussion which followed the paper. Having obtained some very large and clean crystals, I examined them very carefully with the microscope, and found them to be *square* prisms; fortunately, also, I obtained some crystals which appeared to taper to a point when seen by the naked eye. These when magnified could be easily seen to be composed of a number of cubes, arranged in steps and terminating in a single minute cube. Another and conclusive proof of their not belonging to the

rhombic system was the fact that they exerted no action on polarized light.

The fact of there being so complete a change in crystalline form tends, I think, to show that the salt is not a molecular compound.

I hope to be able to obtain similar compounds with the other carbonates which will, no doubt, throw more light on this point.

R. J. F.

XIX.—*On Aurine.*

By R. S. Dale, B.A., and C. Schorlemmer, F.R.S.

Kolbe and Schmitt obtained in 1861 a red colouring matter by heating phenol together with oxalic acid and concentrated sulphuric acid. Since that time this colour has been manufactured, and is found in commerce under the name of *aurine* or *yellow coralline.*

We have commenced an investigation of this body, and found that the commercial product is a mixture, from which we have succeeded in isolating the pure colouring matter. It is best crystallised from strong hot acetic acid, from which it separates on cooling either in splendid chrome-red needles, having a diamond lustre, or in smaller dark red needles with a steel-blue reflexion; often both forms crystallise together from the same solution. Both contain water of crystallisation, which they lose at 160°, assuming at the same time a fine beetle-green lustre.

We have analysed these different bodies and append the numbers, but give the formulæ deduced therefrom with some reserve, as they will have either to be confirmed or to be modified by further research.

The anhydrous compound is $C_{24}H_{18}O_8$.

	Calculated.	Found.	
C.....	66·4	66·7	66·9
H.....	4·2	4·4	4·5

The same body is obtained on boiling the red crystals with such a quantity of glacial acetic acid as will not completely dissolve them. Dark red needles, with a greenish blue lustre, are then left behind.

	Found.	
C.....	66·4	66·6
H.....	4·4	4·5

The red crystals have the composition $C_{24}H_{18}O_8 + 2H_2O$.

	Calculated.	Found.	
C.....	61·3	61·9	61·8
H.....	4·7	5·0	5·3

The steel-blue crystals appear to be $C_{24}H_{18}O_8 + 2\frac{1}{2}H_2O$; dried at 160°, they lost 9·4 and 9·5 per cent. of water; the quantity calculated from the formula being 9·4 per cent.

Kolbe and Schmitt have already stated that the red colour is easily transformed by reducing agents into a colourless body. The best method for effecting this is to heat the red alkaline solution with granulated zinc; the liquid soon becomes colourless, and acids now produce a white crystalline precipitate, crystallising from acetic acid in yellowish thick monoclinic prisms, which are anhydrous and may be heated up to 180° without any alteration of weight. The composition of this compound is $C_{24}H_{20}O_4$.

	Calculated.	Found.	
C.....	77·5	77·6	77·7
H.....	5·4	5·5	5·6

On heating pure aurine with zinc-dust, benzene is produced, besides products having a higher boiling-point. We hope that the study of those, as well as that of the other substances contained in the crude aurine, will give us an insight in the constitution and mode of formation of these different compounds.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

Thermochemical Researches. By JULIUS THOMSEN.*

IX. Specific Heat of Aqueous Solutions.

THE specific heat is estimated by observing the rise in temperature produced in about 900 cub. cent. of the solution, the specific heat of which to be estimated by the combustion, in a suitable calorimeter, of a given volume of hydrogen, and comparing this with the rise produced under like conditions in a known weight of water. The quantities of solution and of hydrogen are chosen so as to give a rise of about 3°. As the hydrogen burns under constant pressure, the temperature rises regularly; and hence, if the temperature of the liquid at the beginning of the experiment is taken as much below the temperature of the air as it will be above it at the end, no corrections are necessary. The accuracy of the method is very great, the differences between the means of several sets of experiments never exceeding 2 per thousand. The results of the experiments, omitting details, are collected in the following tables.

The specific heats refer to a temperature of 18°. Column 1 gives the number of molecules of water (n) present in the solution for one molecule of the substance dissolved; column 2 the specific heat of this solution; column 3 its molecular weight, or, more strictly, the weight corresponding to the chemical formula of the solution. It is given in two terms, the first being the molecular weight of the substance in solution, the second the sum of the weights of the molecules of water. Column 4 gives the molecular heat of the solution, *i.e.*, the products of its specific heat and molecular weight; column 5, the difference between this molecular heat and the heat which would be required by the water of the solution alone; column 6 gives the specific gravity of the solution; column 7, their molecular volume; and lastly, column 8, the difference between 7 and 6.

* Pogg. Ann, cxlii, 337—380.

1. n.	2. Specific Heat.	3. Molecule.	4. Molecular Heat.	5. Difference.	6. Specific Gravity.	7. Molecular Volume.	8. Difference.
		Sulphuric Acid, $SO_3 + nH_2O$.					
5	0·545	80 + 90	92·7	+ 2·7	1·4722	115·5	+ 25·5
10	0·700	80 + 180	182·0	+ 2·0	1·2870	202·0	+ 22·0
20	0·821	80 + 360	361·2	+ 1·2	1·1593	379·6	+ 19·6
50	0·918	80 + 900	900	0	1·0692	916·6	+ 16·6
100	0·956	80 + 1800	1797	− 3	1·0355	1815·5	+ 15·5
200	0·977	80 + 3600	3595	− 5	1·0180	3615·4	+ 15·4
		Nitric Acid, $NO_3H + nH_2O$.					
10	0·768	63 + 180	186·6	+ 6·6	1·1542	210·5	+ 30·5
20	0·849	63 + 360	359·1	− 0·9	1·0851	389·8	+ 29·8
50	0·930	63 + 900	896	− 4·	1·0360	929·5	+ 29·5
100	0·963	63 + 1800	1794	− 6	1·0185	1829·2	+ 29·2
200	0·982	63 + 3600	3597	− 3	1·0094	3629·0	+ 29·0
		Hydrochloric Acid, $HCl + nH_2O$.					
10	0·749	36·5 + 180	162·2	− 17·8	1·0832	199·9	+ 19·9
20	0·855	36·5 + 360	338·9	− 21·9	1·0456	379·2	+ 19·2
50	0·932	36·5 + 900	873	− 27	1·0193	918·8	+ 18·8
100	0·964	36·5 + 1800	1770	− 30	1·0100	1818·5	+ 18·5
200	0·979	36·5 + 3600	3561	− 39	1·0052	3617·7	+ 17·7
		Tartaric Acid, $C_4H_6O_6 + nH_2O$.					
10	0·745	150 + 180	246	+ 66	1·2499	265·9	+ 85·9
25	0·856	150 + 450	513	+ 63	1·1229	534·3	+ 84·3
50	0·911	150 + 900	957	+ 57	1·0677	983·4	+ 83·4
100	0·952	150 + 1800	1856	+ 56	1·0358	1882·5	+ 82·5
200	0·975	150 + 3600	3656	+ 56	1·0186	3681·3	+ 81·3
		Sodium Hydrate, $NaOH + nH_2O$.					
7½	0·847	40 + 135	148·2	+ 13·2	1·2576	139·2	+ 4·2
15	0·878	40 + 270	272·2	+ 2·2	1·1450	270·7	+ 0·7
30	0·919	40 + 540	533	− 7	1·0782	537·9	− 2·1
50	0·942	40 + 900	885	− 15	1·0486	896·4	− 3·6
100	0·968	40 + 1800	1781	− 19	1·0246	1795·9	− 4·1
200	0·983	40 + 3600	3578	− 22	1·0124	3594·8	− 5·2

1. n.	2. Specific Heat.	3. Molecule.	4. Molecular Heat.	5. Difference.	6. Specific Gravity.	7. Molecular Volume.	8. Difference.
		Potassium Hydrate, $KHO + nH_2O$.					
30	0·876	56 + 540	522	− 18	1·0887	547·5	+ 7·5
50	0·916	56 + 900	876	− 24	1·0550	906·3	+ 6·3
100	0·954	56 + 1800	1770	− 30	1·0284	1804·9	+ 4·9
200	0·975	56 + 3600	3565	− 35	1·0144	3604·1	+ 4·1
		Ammonium Hydrate, $NH_4.OH + nH_2O$.					
30	0·997	35 + 540	573	+ 33	0·9878	582·1	+ 42·1
50	0·999	35 + 900	934	+ 34	0·9927	941·9	+ 41·9
100	0·999	35 + 1800	1833	+ 33	0·9967	1841·2	+ 41·2
		Sodium Chloride, $NaCl + nH_2O$.					
10	0·791	58·5 + 180	188·5	+ 8·5	1·1872	200·9	+ 20·9
20	0·863	58·5 + 360	361·0	+ 1·0	1·1033	379·3	+ 19·3
30	0·895	58·5 + 540	536	− 4	1·0718	558·4	+ 18·4
50	0·931	58·5 + 900	892	− 8	1·0444	917·8	+ 17·8
100	0·962	58·5 + 1800	1788	− 12	1·0234	1816·1	+ 16·1
200	0·978	58·5 + 3600	3578	− 22	1·0118	3616·0	+ 16·0
		Potassium Chloride, $KCl + nH_2O$.					
15	0·761	74·6 + 270	262·4	− 7·6	1·1468	300·4	+ 30·4
30	0·850	74·6 + 540	522·4	− 17·4	1·0800	569·0	+ 29·0
50	0·904	74·6 + 900	881	− 19	1·0496	928·2	+ 28·2
100	0·948	74·6 + 1800	1775	− 25	1·0258	1827·3	+ 27·3
200	0·970	74·6 + 3600	3565	− 35	1·0136	3625·0	+ 25·0
		Ammonium Chloride, $NH_4Cl + nH_2O$.					
7½	0·760	53·5 + 135	143·3	+ 8·3	1·0718	175·9	+ 40·9
10	0·778	53·5 + 180	181·6	+ 1·6	1·0664	219·0	+ 39·0
25	0·881	53·5 + 450	443·6	− 6·4	1·0314	488·2	+ 38·2
50	0·937	53·5 + 900	893	− 7	1·0167	937·8	+ 37·8
100	0·966	53·5 + 1800	1791	− 9	1·0086	1837·7	+ 37·7
200	0·982	53·5 + 3600	3588	− 12	1·0044	3637·6	+ 37·6
		Sodium Nitrate, $NaNO_3 + nH_2O$.					
10	0·769	85 + 180	203·8	+ 23·8	1·2474	212·5	+ 32·5
25	0·863	85 + 450	461·7	+ 11·7	1·1137	480·4	+ 30·4
50	0·918	85 + 900	904	+ 4	1·0600	929·2	+ 29·2
100	0·950	85 + 1800	1791	− 9	1·0311	1828·2	+ 28·2
200	0·975	85 + 3600	3593	− 7	1.0160	3627·0	+ 27·0

1. n.	2. Specific Heat.	3. Molecule.	4. Molecular Heat.	5. Difference.	6. Specific Gravity.	7. Molecular Volume.	8. Difference.
		Potassium Nitrate, $KNO_3 + nH_2O$.					
25	0·832	101 + 450	458·4	+ 8·4	1·1228	490·7	+ 40·7
50	0·901	101 + 900	902	+ 2	1·0651	939·8	+ 39·8
100	0·942	101 + 1800	1791	− 9	1·0336	1839·2	+ 39·2
200	0·966	101 + 3600	3575	− 25	1·0173	3638·3	+ 38·3
		Ammonium Nitrate, $NH_4.NO_3 + nH_2O$.					
5	0·697	80 + 90	118·7	+ 28·7	1·2046	141·1	+ 51·1
20	0·859	80 + 360	378·0	+ 18	1·0743	409·6	+ 49·6
50	0·929	80 + 900	910	+ 10	1·0331	948·6	+ 48·6
100	0·962	80 + 1800	1808	+ 8	1·0180	1846·8	+ 46·8
		Sodium Carbonate, $Na_2OCO_3 + nH_2O$.					
50	0·896	106 + 900	901	+ 1	1·1131	903·8	+ 3·8
100	0·933	106 + 1800	1778	− 22	1·0593	1799·3	− 0·7
200	0·958	106 + 3600	3550	− 50	1·0396	3596·0	− 4·0
		Sodium Sulphate, $Na_2O.SO_3 + nH_2O$.					
65	0·892	142 + 1170	1170	0	1·1010	1191·6	+ 21·6
100	0·920	142 + 1800	1787	− 13	1·0675	1819·5	+ 19·2
200	0·955	142 + 3600	3574	− 26	1·0350	3615·4	+ 15·4
		Ammonium Sulphate, $Am_2O.SO_3 + nH_2O$.					
30	0·820	132 + 540	551	+ 11	1·1148	602·8	+ 62·8
50	0·871	132 + 900	899	− 1	1·0774	957·6	+ 57·6
100	0·924	132 + 1800	1785	− 15	1·0420	1854·1	+ 54·1
200	0·959	132 + 3600	3579	− 21	1·0214	3653·8	+ 53·8
		Magnesium Sulphate, $MgO.SO_3 + nH_2O$.					
20	0·744	120 + 360	357	− 3	1·2864	373·1	+ 13·1
50	0·857	120 + 800	874	− 26	1·1253	906·4	+ 6·4
100	0·917	120 + 1800	1761	− 39	1·0649	1803·0	+ 3·0
200	0·952	120 + 3600	3541	− 59	1·0334	3599·8	− 0·2

1. n.	2. Specific Heat.	3. Molecule.	4. Molecular Heat.	5. Difference.	6. Specific Gravity.	7. Molecular Volume.	8. Difference.
		Sodium Acetate, $NaOC_2H_3O + nH_2O$.					
20	0·884	82 + 360	391	+ 31	1·0993	402·1	+ 42·1
50	0·938	82 + 900	921	+ 21	1·0442	940·4	+ 40·4
100	0·965	82 + 1800	1817	+ 17	1·0230	1839·7	+ 39·7
200	0·983	82 + 3600	3620	+ 20	1·0120	3638·3	+ 38·3
		$n + 200H_2O$.					
1.	2.	3.	4.	5.	6.	7.	8.
KBr	0·962	119 + 3600	3578	− 22	1·0236	3633	+ 33
AmBr	0·968	98 + 3600	3580	− 20	1·0154	3642	+ 42
NaI	0·954	150 + 3600	3578	− 22	1·0318	3634	+ 34
KT	0·950	166 + 3600	3578	− 22	1·0355	3644	+ 44
AmI	0·963	145 + 3600	3606	+ 6	1·0248	3654	+ 54
$BaCl_2$	0·932	208 + 3600	3549	− 51	1·0502	3626	+ 26
$CaCl_2$	0·957	111 + 3600	3551	− 49	1·0253	3619	+ 19
K_2O,SO_3	0·940	174 + 3600	3548	− 52	1·0380	3636	+ 36
ZnO, SO_3	0·947	161 + 3600	3562	− 38	1·0455	3598	− 2
FeO,SO_3	0·951	152 + 3600	3568	− 32	1·0413	3603	+ 3
CuO,SO_3	0·953	159 + 3600	3583	− 17	1·0444	3599	− 1
BaO,N_2O_5	0·933	261 + 3600	3602	+ 2	1·0584	3648	+ 48
PbO,N_2O_5	0·919	331 + 3600	3613	+ 13	1·0771	3649	+ 49

The numbers in column 4 of the preceding tables express the water-value of the solution, that is, the weight of water which requires the same amount of heat as the molecular weight of solution, and a glance at the table shows that this water-value differs in most cases but little from the amount of water present in the solution. In the case of sulphuric acid, for example, the solution with 5 molecules of water has a water-value of 92·7, the weight of the molecules of water in the solution being 90, that of the whole molecule 170; in the solution with 50 molecules of water, these values are 900, 900, and 980 respectively, while, in still more dilute solutions, the water-value sinks even below the molecular weight of the water actually present. Similar phenomena are observed in most other solutions; the differences in column 5 are generally positive in concentrated solutions, gradually sink to zero, and become negative in dilute solution. In some few cases, as with hydrochloric acid and potassium hydrate, they are always negative.

Undoubtedly the specific heat of aqueous solutions stands in intimate relation to their chemical composition, but before more is known of the molecular changes taking place during solution, no formula can be given embracing more than two or three characteristics, and until all can thus be embraced, such formulæ have but little interest.

Between some of the characters, however, the connection is very striking, as for example, between the molecular heat and the molecular volume of a solution.

Previous researches by other experimenters, as well as those of the author, have shown that contraction takes place when an aqueous solution is mixed with water, *i.e.*, the volume of the solution is less than the sum of the volumes of the constituent liquids, and the foregoing experiments show that when an aqueous solution is mixed with water, the resulting solution has a lower molecular heat than the sum of the molecular heats of the constituents. A similar relation is found when acids and alkalis are mixed. When potash or soda is neutralized with hydrochloric, nitric, or sulphuric acid, the molecular heat of the resulting compound is higher than the sum of the molecular heats of the constituents, while on the other hand it is found that these potassium and sodium salts have a molecular volume greater than the sum of the volumes of their constituents; in other words, expansion has taken place during combination. In the case of ammonia salts the reverse takes place. Contraction is the result of the combination, and the molecular heat of the compound is less than the sum of the molecular heats of the constituents. A. D.

On the Heat of Neutralisation of Inorganic and Organic Bases soluble in Water. By JULIUS THOMSEN.*

THE author has determined the heat which is produced when a solution of the hydrates of potassium, sodium, lithium and thallium, containing 400 molecules of water to every two of the hydrate is neutralised with sulphuric hydrate containing 400 molecules of water for every molecule of the acid. The thermic reaction of the neutralisation is expressed by the formula, ($2ROH.aq,SO_4H_2.aq$), in which R signifies an atom of the metal. The results of the experiments, which were extended to the metals barium, strontium, calcium and magnesium, are given in the two following lists:—

R	$2ROH.aq,SO_4H_2.aq.$	R	$RO_2H_2.aq,SO_4H_2.aq.$
Li ..	31290 heat units.	Ba ..	31290 heat units.
Na..	31040 ,,	Sr ..	31100 ,,
K ..	31050 ,,	Ca ..	31040 ,,
Tl ..	31140 ,,	Mg..	31130 ,,

On account of the insolubility of magnesium hydrate, the number for magnesium in the second list was determined indirectly by precipitating the solution of the sulphate with potassium and barium

* Deut. Chem. Ges. Ber., iv, 308.

hydrate. The author points out the importance of these numbers:—Firstly, they are almost identical, as the greatest deviation from the mean 31,140 heat-units amounts to only 5 per 1,000; secondly, the numbers of the alkalis agree with those of the alkaline earths; and finally, magnesium is, by its behaviour, allied with the other hydrates mentioned. It may thence be concluded that the molecule of sulphuric hydrate always furnishes the same amount of heat, namely 31134 units, with whatever hydrate of the alkalis or alkaline earths it is neutralised.

The oxides of lead and of silver give different numbers, 18,750 and 14,040 heat-units; and, moreover, the eight bases of the two lists when neutralised with other acids than sulphuric hydrate, do not always appear to belong to the same group. Thus thallium gives with hydrochloric and sulphydric acids, the same numbers as silver; so that similarity in the evolution of heat seems to require similarity in the chemical process.

Ammonia and ethylamine gave numbers which are considerably lower than might have been expected, if the ammonium theory holds good in the case of the aqueous solutions of these substances; and the author considers this as a strong proof that the constitution of these solutions is really quite different from that of the inorganic hydrates of the alkalis.

The number found for tetramethylammonium hydrate is 31,010, and seems, therefore, to confirm the supposed analogy between these organic ammonium bases and the hydrates of the inorganic bases.

The heat evolved on mixing stibethy oxide with sulphuric hydrate or with the halogen acids was very inconsiderable, only about one-tenth of that obtained with the other bases; it seems, therefore, that this body possesses a constitution different from that of the previously mentioned organic bases, and that its compounds with the hydrated acids will perhaps have to be considered as double salts.

The author proposes to extend this research to a greater number of organic bases.

R. S.

On the Heat evolved in the Formation of Aqueous Solutions.
By Friedrich Mohr.*

The author traces the heat which has either been evolved or absorbed in the act of chemical combination in the new qualities of the product, which in the first case possesses higher melting and boiling points, and less volatility than the mean of the constituents, and in the second case has lower melting and boiling points, and is less easily fusible.

Generally, the fall of temperature occasioned by the solution of a

* Deut. Chem. Ges. Ber., iv, 314.

salt in water, or by mixing a salt with snow, is ascribed to a change in the state of aggregation. Mohr, however, referring to the fact that a fall of temperature is also observed when an aqueous solution of common salt is mixed with an additional quantity of water—when no liquefaction takes place—thinks that this explanation does not account for the whole loss of heat, but that part of the heat disappears and becomes latent, or enters the body in such a manner as to give rise to a new permanent quality, namely, lower freezing point.

R. S.

On the Variations of the Coefficient of Expansion of Gases.
By M. E. H. Amagat.*

The author has estimated the rate of expansion of sulphurous and carbonic anhydride, by direct comparison with atmospheric air, between the temperatures 10—60°, 10—100°, 10—150°, 10—200°, and 10—250°; the expansion for intermediate temperatures being afterwards found by interpolation. The following table gives the results obtained with sulphurous anhydride for every 10 degrees up to 50°, and for every 25° up to 250°, air having, between these limits, the constant co-efficient of 0·00367.

Sulphurous anhydride.

From	0° to 10°	0·004220	From	100° to 125°	0·003786
,,	10 to 20	·004005	,,	125 to 150	·003771
,,	20 to 30	·003930	,,	150 to 175	·003760
,,	30 to 40	·003890	,,	175 to 200	·003754
,,	40 to 50	·003863	,,	200 to 225	·003750
,,	50 to 75	·003830	,,	225 to 250	.003748
,,	75 to 100	·003806			

The expansion between 0 and 10° was not estimated directly, but was calculated from the expansion between 0 and 100° given by Regnault, and that between 10 and 100° found by the author.

In the case of carbonic anhydride the differences in the rate of expansion are much less than they are for sulphurous anhydride, and considerable ranges of temperature must be taken in order to obtain sensible differences in the coefficients. Thus, between 0° and 100° Regnault found the co-efficient 0·00371, between 0° and 200° the author found a co-efficient of 0·003704, and, practically, the same co-efficient was obtained between 0 and 250°. Each number is the mean of 10 or 12 experiments, as closely concordant as could be expected. Moreover their accuracy is readily checked by introducing the same gas into the two cylinders of the apparatus when the same numbers are found. In the case of air, for example, the mean of four experiments with one cylinder was 0·00367, the mean of four similar experiments with the second cylinder being 0·003671 (the last four experiments giving 0·003667, 0·003671, 0·003673, and 0·003673; mean 0·003671).

* Arch des Sciences phys. et natur. [2], iv, 320.

The co-efficient of expansion of sulphurous anhydride decreases with increasing temperature, at first rapidly, up to a temperature of 50°, and then slowly, up to about 250°, above which it apparently remains constant. It seems, therefore, that the coefficient tends towards a limit which differs from that of atmospheric air, namely 0·00374. Carbonic anhydride shows a similar result; the coefficient diminishes, though slightly, up to about 200°, above which temperature it appears to remain constant at 0·003695, or also slightly higher than that of atmospheric air.

The author finally advances the following theory. The coefficient of expansion of each gas reaches a certain limit, which limit is different for each gas, and depends on the complexity of the molecular constitution of the gas, the coefficient being the greater the greater this complexity. A. D.

On the Determination of the Melting and Solidifying Points of Fats.
By Th. Wimmel.*

The author, finding his method and those of others, of determining melting points, objected to by Ruedorff, on the ground that according to his results, the point of melting would not be the same as the point of solidifying, makes some remarks on the fact that some fats may be made to solidify at two different temperatures.

When fats which yield glycerin by saponification are allowed to cool whilst in the melted state, their temperature, after first sinking, becomes constant for a time, and then exhibits a sudden rise. This occurs at a definite point for each fat, which is, therefore, called the "natural" point of solidification, although the state of the fat at the time may be considered as abnormal (*Ueberschmelzung*—superfusion?) The process by which Ruedorff has succeeded in raising the freezing point so far as to make it almost coincide with the melting point, can only be called an artificial one. Other fats exhibit only one point of solidification which coincides with the melting point.

The author thinks that the solidifying point, which he calls the natural one, though it is different from the melting point, should be more regarded than it has been hitherto, as it is more constant, and allows of an easier determination than the other.

R. S.

On the Thermo-Electric Action of Liquids and Metals.
By George Gore, F.R.S.†

The object of Mr. Gore's researches was the further investigation of the relations of the temperature and chemical action of metals to their electrical state. The metal chiefly examined was copper. Two shallow dishes connected by wires with a suitable galvanometer, were so

* Pogg. Ann., cxlii, 471—474. † Proc. Roy. Soc. xix. 324—345.

arranged in a U-shaped glass vessel with vase-like terminations, that the under surfaces of both could be placed in contact with any active liquid contained in the glass vessel. The author in his experiments heated one of the copper dishes by pouring hot water into it, the other remaining at the temperature of the atmosphere. The general results are as follow:—The hot copper dish was positive to the cold one, the active liquids were: hydrochloric, hydrocyanic, boric, and orthophosphoric acids; cupric chloride (weak solution); cobalt chloride; manganous chloride; chromic acid; chromic chloride; zinc sulphate (weak solution); magnesium sulphate; calcium chloride; strontium nitrate and chloride; barium chloride; sodium nitrate (strong solution); sodium chloride, iodide, carbonate, and diborate; sodium sulphate (strong solution); trisodic phosphate; potassium nitrate, chloride, and chlorate; potassium bromide (strong solution); potassium iodide (strong solution); potassium carbonate, hydrocarbonate and dichromate; ammonium hydrate and chloride; potassium cyanide and ferro-cyanide; zinc acetate; and sodium acetate. Negative in the following: nitric, chloric, hydrobromic, hydrofluosilicic, and sulphuric acids; ferrous sulphate; cupric chloride (strong solution); cupric sulphate; zinc sulphate (strong solution); sodium nitrate and iodide (weak solutions); potassium iodate; chrome-alum; ammonium nitrate; oxalic, acetic, tartaric, and citric acids. In several instances where the hot metal was negative with a weak solution, it became positive in a strong one. The direction of the current appeared to be more influenced by the nature of the acid in a salt than by that of the base. Mr. Gore considers the currents in all his experiments of difference of temperature to be due either "(1) to the direct influence of heat, the effect of which would be to make the hot copper negative in acid, and positive in alkaline liquids; (2) to chemical action, which sometimes overpowers the direct influence of heat and reverses the effect; or, (3) to both these influences combined." The action of air in promoting oxidation at the line where the liquid and metal come in contact with it, no doubt influences the amount of current, as also perhaps the direction. Mr. Gore instituted some experiments to elucidate this matter, and found that when the air-line was long, the metal became electro-negative in all cases, and gave stronger indications when the liquid had a powerful *chemical* action.

To ascertain whether the quantity of current was due to the difference in number of the molecules of liquid touching the hot and cold plates respectively, and also what amount of difference of strength of liquid was equivalent to the difference of temperature employed, the author worked with liquids of unequal strength, instead of unequal temperature. The results arrived at show that heat does not

act simply by causing a greater number of molecules of each substance to touch the hot plate.

Following the suggestions of these researches, the author constructed a thermo-electric battery, using acid and alkaline liquids in separate glass tubes, having platinum wires fused into their extremities. These tubes were so arranged that one end of each could be heated. To understand the precise construction of the instrument and the manner of connecting the platinum wires, it is necessary to examine the sketch in the original paper. The quantity of electricity produced by this instrument was small, but the intensity considerable. By employing electrodes of larger surface and concentrated liquids, the quantity could be largely increased.

The influence of friction was also examined, and the experiments showed that the molecular movements produced by friction are not in all cases similar to those produced by heat.

The author has also ascertained that the thermo-electric properties of liquids are not dependent on the molecular structure by virtue of which, liquids under the influence of magnetism polarize light circularly.

From these investigations Mr. Gore draws the following general conclusion:—"The electric currents produced by the direct influence of unequal temperature or friction of platinum or copper electrodes, in conducting liquids which do not act chemically upon those metals, have their origin in temporary changes of cohesion of the layers of metal and liquid which are in immediate and mutual contact, and may be considered a very delicate test of the kind and amount of temporary molecular movements produced by those causes."

S. W.

On the Increase of Electrical Resistance in Conductors with Rise of Temperature, and its application to the Measure of Ordinary and Furnace Temperatures; also on a simple Method of measuring Electrical Resistance. By CHARLES WILLIAM SIEMENS.

DR. SIEMENS, in the first part of his paper, treats of the rate of increase of electrical resistance in metallic conductors under an increase of temperature. The tabulated results of his experiments show that this ratio is represented by the ordinate of a parabola, modified by two other terms depending on linear expansion and ultimate minimum resistance; thus it is not a uniform progression nor does it conform to Dr Matthiessen's formula, except within the narrow limits of his experiments. The author has used in his investigations different metals, including platinum, copper, and iron. In one set of observations the range of temperature extended from 0° to 350°, and in another it reached as high as 1000°.

Assuming that the electrical resistance of a conductor increases according to the velocity with which the atoms are moved by heat, a parabolic ratio of increase of temperature follows. Adding the terms above mentioned, the resistance r for any temperature may be expressed in the equation:—

$$r = \alpha T + \beta T^{\frac{1}{2}} - \gamma.$$

This formula closely represents the results of experiment.

Taking advantage of these circumstances, Dr. Siemens shows in the second part of his paper, that an instrument may be constructed capable of measuring temperature in distant or inaccessible places, including the interior of furnaces. For measuring temperatures not exceeding 100°, two similar coils are connected by a light cable, containing three insulated wires. One of these coils, "the thermometer coil," carefully protected against moisture, may be lowered into the sea, buried in the ground, or conveyed into any place of which it is desired to ascertain the temperature. The other coil, "the comparison coil," is placed in a test-bath, whose temperature may be raised or lowered at pleasure, until an electrical balance is established between the resistances of the two coils. This may be ascertained by means of a galvanoscope, or a differential voltameter, such as the author describes in the third part of his paper, of which an abstract will be found below. The temperature of the test-solution, found by a delicate mercurial thermometer, gives the temperature of the thermometer coil.

The comparison coil may be dispensed with when the resistance of the thermometer coil at 0°—which is a constant quantity—is known. A table of temperatures corresponding with the indications of the instrument saves the trouble of calculation. The third wire in the cable, being common to both branches of the measuring instrument, eliminates all disturbing influence, which would be considerable when a great length of wire was used.

For measuring furnace temperatures, a platinum wire wound round a cylinder of porcelain forms the thermometer coil, and the whole is inclosed in an iron or platinum tube. When temperatures not exceeding 1000° are to be measured, the instrument may be left permanently in the furnace. At higher temperatures, it must be introduced for a definite time, sufficient to give the casing and wire, within a determinable limit, the temperature to be measured, but not sufficient to soften the porcelain cylinder on which the platinum is coiled.

The third part of the paper is devoted to the description of a differential voltameter. It consists of two tubes fixed upon graduated scales, which are so arranged that the current of a battery is divided between them, one branch including a known and permanent resistance, and the other the unknown resistance to be measured. The resistance and polarization being equal, and the battery being common to both

circuits, these unstable elements are eliminated by balancing them for the circulation; and an expression is found for the unknown resistance, X, in terms of the known resistance, C and γ of the voltameter, including the connecting wires; and of the volumes V and V′ of gases evolved in the voltameter in any convenient space of time:—

$$X = \frac{V}{V'} (C + \gamma) - \gamma.$$

Changes of pressure affect both sides equally; a reading, however, at atmospheric pressure may be obtained by lowering the little supply reservoir with dilute acid to the level indicated in the corresponding tube. The upper ends of the tubes are closed with india rubber valves which may be raised and the gases allowed to escape, until the liquid is brought back to the zero point of the scale. The instrument is not influenced by magnetic disturbances or by a ship's motion, and can be used by persons not familiar with electrical testing.

S. W.

L. Kohlfürst's *improved Copper-Zinc Battery.**

The zinc is cast in the form of a thick cake with three arms attached, by means of which it can be suspended in a glass cylinder, one arm carries a clamping screw. The cake is pierced in the centre, and its lower surface is slightly spherical. A truncated hollow cone of hammered copper serves as the negative plate. The cone is about one half the height of the glass cylinder; it is open below, closed above, with the exception of a small hole in the centre. The outside, for a breadth of about an inch and a half round the lower rim, and the whole of the inside are strongly varnished. Three or four notches are cut into the lower rim. A copper wire covered with gutta-percha is soldered to the cone, and passes up through the hole in the zinc cake. To charge the battery, the cone is filled with crystals of copper sulphate, the glass is placed over it, mouth downwards, and then inverted; the zinc cake is now hung in, and the cylinder filled with pure water, or, if greater strength is required, with a dilute solution of magnesium sulphate or sodium chloride. The rate at which the copper sulphate dissolves, and consequently the strength of the current, may be regulated by the size of the notches cut into the rim. The current remains constant until the crystals have been dissolved down to the upper margin of the notches. If the battery is employed for ringing ordinary electric bells, a cone holding $1\frac{1}{2}$ lb. of crystals will keep it going for about a year.

A. D.

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* Dingl. Pol. J., cc, 103.

On the Electromotive and Electrolytic Phenomena developed by Gold and Platinum in Solutions of the Alkaline Sulphides and Sulphuretted Hydrogen. By WILLIAM SKEY.*

THE author states that electric currents of considerable intensity are developed by either gold or platinum under the following circumstances:—

Two plates of gold (prepared chemically pure) are taken; one is placed in a cell partly filled with sea water, and the other in a porous cell containing ammonium sulphide, or sea water charged with hydrogen sulphide. On making connection, a strong current passes from the gold plate in the inner cell to that in the outer, the electric currents obtained in this way being able to decompose solutions of gold, silver, and copper.

To avoid the electromotive action described by Becquerel, the author previously boils the solutions to expel the air from them, and immerses the plates of gold or platinum, while red hot, in the solutions.

If potash or ammonia be substituted for ammonium sulphide, the currents obtained are very much weaker.

C. G.

Chemical and Mechanical Changes of the Silver Haloid Salts by Light. By C. SCHULTZ-SELLACK.†

BY exposure to light, silver chloride and bromide become much darker coloured, whilst free chlorine and bromine can be detected. In the case of silver iodide the colour darkens considerably, but no free iodine can be recognized. Schultz-Sellack supposes that these changes are due to dissociation caused by the light, and reasoning on this, hoped to be able to detect free iodine from silver iodide exposed to light at a higher temperature; no free iodine could however be found, although the salt became very much darker. In the dark, the haloïd silver salts can easily be obtained in transparent crystals, the bromide and chloride from their solutions in ammonia, and the iodide from hydriodic acid. If these are placed in tubes in presence of free bromine, chlorine, and iodine respectively, and exposed to the action of light, no chemical change takes place, but a mechanical one is observed. The silver iodide crystals fall to powder, whilst the chloride and bromide crystals become opaque and lose their brillancy. The transparent layer of silver iodide formed by iodizing a silver surface, changes in a few minutes in sunlight to a yellow-grey rough mass, which shows by transmitted light different colours according to the length of the action; first, it appears yellow-brown, then dark brown, then red, green, and blue, and finally

* Chem. News, xxiii, 221.

† Deut. Chem. Ges. Ber., iv, 343.

of a bluish white. These colours are caused by diffraction, and seem to depend on the fineness of the silver iodide powder; if the layer be varnished, it changes its colour and loses a great part of its intensity. The mechanical changes of silver iodide are caused only by those colours of the spectrum which act on it photographically. By exposure under a photographic negative, a positive picture is first produced, but by allowing the action to continue longer, it passes through beautiful gradations of colour into a negative. Schultz-Sellack concludes that the photographic process is inseparably connected with the chemical decomposition, and that the mechanical change of the silver haloïd salts in the photographically sensitive condition is completely parallel to the chemical change, but that it is very small.

A. P.

On Fluorescence. By F. GOPPELSRÖDER.*

WHEN equal volumes of strong sulphuric acid and pure ethyl-alcohol are warmed together, the mixture exhibits a greenish-yellow fluorescence, which is observed also in an alcoholic extract of the carbonaceous mass, left on evaporating the liquid till sulphur dioxide is freely evolved. A mixture of equal volumes of methyl alcohol and sulphuric acid exhibits the same phenomenon, the upper layer, which consists of methyl alcohol, being colourless. On warming equal volumes of sulphuric acid and amyl alcohol, the former is coloured yellow, orange, and carmine-red, and exhibits a greenish-yellow fluorescence, especially after dilution with ordinary alcohol.

J. R.

A Lecture Apparatus for Specific Gravities. By J. Y. BUCHANAN.†

THIS is an apparatus for exhibiting the specific gravity of solid bodies, and consists simply of a rather large Nicholson's Hydrometer, the total length being 80 centimetres. The stem is 36 centimetres long by 7 millimetres in diameter, and is graduated so that each division represents 1 cubic centimetre of water, thus giving the weight of the body placed in the upper scale pan in grams by simple inspection. The apparatus is used in a manner precisely similar to Nicholson's hydrometer.

C. E. G.

On a new Manometer for Measuring High Pressures of Gases. By V. REGNAULT (Archiv. des Sciences [2], iv, 311).

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* Zeitschr. f. Chem. [2], vii, 91, from Zeitschr. Anal. Chem., 1870, 178.

† Deut. Chem. Ges. Ber., iv, 338—340.

On the apparent Expansion of Mercury, and on the Comparison of the Mercurial and Air Thermometers, according to Regnault's Experiments. By J. BOSSCHA, jun. (Pogg. Ann. Ergänzungsband v, 444).

On the Boiling Points of Organic Bodies. By F. BURDEN (Phil. Mag. [4], xli, 528).

On the Transformations of the Spectra of Incandescent Gases due to Changes of Pressure and Temperature. By A. WÜLLNER (Archiv. des Sciences [2], iv, 305).

Inorganic Chemistry.

Considerations on the System of the Elements. By D. MENDELEJEFF (Deut. Chem. Ges. Ber., iv, 348).

On the Conjugated Compounds of Pentatomic Nitrogen. By C. W. BLOMTRAND (J. pr. Chem. [2], iii, 186—224).

Formation of Ozone in Rapid Combustion. By C. THAN.*

THE author attempted to demonstrate Schönbein's observation that ammonium nitrite is formed in the combustion of hydrogen or hydrogenous substances by drawing air from the lower edge of the flame of a Bunsen burner through an acidulated solution of potassium iodide and starch. A blue coloration was speedily produced, but it was noticed at the same time that the air in the vessel containing the solution smelt distinctly of ozone. Pure water was then substituted for the foregoing solution, and a prolonged current of air from the lower edge of the flame drawn through it. On testing the liquid with potassium iodide and starch, no blue colour was produced, showing that ammonium nitrite was not present. The coloration in the first experiment was therefore due to ozone. Than succeeded in obtaining ozone also from the flames of hydrogen, of candles, and of a spirit-lamp. The air must be rapidly drawn directly from the lower edge of the flame, where cold air impinges upon it, the tube used for the purpose having a diameter of about 1 mm.; but the current must not be so strong as to draw the flame itself into the tube, otherwise the ozone is completely destroyed by the combustible gases. Ozone is also formed when a strong current of air is blown through the upper part of the flame. It is produced

* Zeitschr. f. Chem. [2], vii, 92, from J. pr. Chem. [2], i, 415.

in the combustion of hydrogenous substances only, not of carbon. The author gives the following explanation of his observations. Ozone, according to Clausius and Soret, is represented by the formula O_3. Now in the combustion of hydrogen one molecule of that element is capable of separating the two atoms of a molecule of oxygen, one of which combines with the hydrogen to form water, whilst the other may unite with a molecule of oxygen to form ozone, thus :—

$$H_2 + O_2 = H_2O + O\,;\ O + O_2 = O_3.$$

It is not surprising that no ozone is formed in the combustion of carbon, seeing that an atom of carbon is capable of combining with an entire molecule of oxygen.

J. R.

On the Existence and Formation of Salts of Nitrous Oxide. By EDWARD DIVERS.*

METALLIC sodium thrown on to a solution of an alkali nitrate was found by Schönbein to reduce it to nitrite. By using the sodium in the form of amalgam, the complete reduction of the nitrate can be readily effected. But the nitrite, so soon as it is thus formed by the sodium, begins itself to suffer reduction. Among the products of this reduction, Fremy has recognized oxyammonia, nitrogen, and nitrous oxide, and Maumené has found ammonia. But the principal, and sometimes the sole, products are nitrous oxide, a new salt—sodium hyponitrite, NONa, and by necessary inference, sodium oxide—

$$2NONa = N_2O + ONa_2.$$

When ammonium nitrate is employed, no ammonium amalgam is formed, sodium salts are produced, ammonia is liberated, and the reductions proceed as when sodium nitrate is taken.

To prepare hyponitrites, or salts of nitrous oxide, the solution of nitrate is treated in a flask with an amalgam of four or more atoms of sodium, the solution being kept cool by immersing the flask in cold water. The very alkaline product is then treated with acetic or weak nitric acid until the liquid no longer gives a brown or black precipitate with silver nitrate. Excess of acid must be avoided, except when the silver salt of the new acid is to be prepared, when excess of acetic acid is of little consequence.

The silver salt alone has as yet been analysed, and this in a condition not quite pure. The results of the analysis, however, indicate a composition expressed by the formula, NOAg.

The following reactions have been obtained with the neutralised solution.

It is *alkaline* to test-paper. The alkalinity of the sodium salt is

* Proc. Roy. Soc., xix, 425—431.

further shown, firstly, by silver nitrate giving with the solution the silver salt of the new acid and a neutral mother-liquor, and secondly, by the washed silver salt giving with sodium chloride an alkaline liquid, and pure white silver chloride. Ammonium chloride gives a similar reaction with the silver salt, but the solution smells of ammonia.

Silver nitrate gives a yellow, pulverulent precipitate, insoluble in water, almost insoluble in acetic acid, insoluble in and undecomposed by sodium hydrate and carbonate, soluble in ammonia, ammonium carbonate, nitric acid and sulphuric acid, and decomposed by hydrochloric acid, hydrosulphuric acid, alkaline chlorides and sulphides. From its solution in ammonia, the silver salt can be re-obtained by the volatilization of the ammonia, or by the cautious addition of nitric acid, or by addition of acetic acid even in excess. It can also be re-obtained from its recently made solution in dilute nitric acid or sulphuric acid by adding excess of sodium hydrate or carbonate, or just sufficient ammonia or ammonium carbonate. It is decomposed, with effervescence, by moderately strong sulphuric acid, the products being apparently nitrogen, nitrous, and nitric acids. Moderately strong nitric acid appears to have the same effect as sulphuric acid. Strong nitric acid decomposes it with copious production of red fumes. It can be heated nearly to 100° C. without decomposition. Boiled in water, it is decomposed. Heated to 100° or higher, it is decomposed without fusion into metallic silver, a little silver nitrate and nitric oxide.

Cupric sulphate gives a yellowish, olive-green, flocculent precipitate, soluble in acids and ammonia, insoluble in sodium hydrate, and unaffected by boiling in water or its mother-liquor. *Lead acetate* gives a cream-white, flocculent precipitate which generally on standing changes to a very dense, full yellow precipitate, unchanged by boiling, soluble in acids, apparently unaffected by sodium carbonate or ammonia, and instantly decomposd by caustic soda. *Mercuric chloride* gives a cream-white, flocculent precipitate. *Mercurous nitrate* gives a blackish-grey precipitate, not improbably a mixture of mercury and the mercuric salt. *Nickel chloride* gives a greenish, almost white precipitate, and *manganese chloride* a nearly white one. *Alum* gives a white precipitate, and slow effervescence. *Ferric chloride* gives a slight, reddish-brown precipitate; and *ferrous sulpate*, a whitish precipitate instantly darkening to dirty blackish green, and eventually reddish brown. Both precipitants cause languid effervescence. These precipitates and that given by alum are not improbably only hydrates of the respective metals. *Zinc chloride* gives a white precipitate. *Barium chloride* gives no precipitate. The acidified solution gives no coloration with *ferrous sulphate*, until poured on to concentrated sulphuric acid. The

acidified solution does not appear to reduce *potassium dichromate*. *Potassium permanganate* gives with the neutral solution the beautiful changes of colour from its own violet, through purple, blue, and chrome-green, to manganese-green, and then a brown precipitate. It is immediately reduced by the acidified solution. *Potassium iodide* gives no reaction, not even after acidification with acetic or hydrochloric acid (not nitric acid). *Iodine solution* is immediately decolorised, even without the addition of an acid. The presence, therefore, of nitrite, not in excess, is masked by the presence of the new salt when the potassium iodide test is employed. For the iron, iodine, and iodide of potassium tests, the neutralisation of the caustic soda must be effected by acetic acid and not by nitric acid.

The original alkaline liquid acidified with acetic acid and heated evolves nitrous oxide (hyponitrous anhydride), thus :—

$$2NOH = N_2O + OH_2.$$

There is good reason to believe that the yellow insoluble matter obtained in small quantity by heating silver nitrite is the silver salt of nitrous oxide.

Some good commercial sodium nitrite has been found by the author to give apparent indications of the presence of a minute quantity of sodium hyponitrite.

Hess obtained what appears to have been silver hyponitrite by heating barium nitrate, treating the product with silver salt and decomposing some crystals thus obtained by water.

Lastly, Sir H. Davy obtained what he believed to be the potassium salt of nitrous oxide by acting on solid potassium hydrate and sulphite with nitric oxide. The product evolved pure nitrous oxide when heated. Pelouze's nitrosulphates, obtained in a somewhat similar manner, evolve nitric oxide when heated.

The author is occupied with a fuller investigation of this interesting class of salts.

E. D.

On the Specific Gravity of Aqueous Hydrobromic Acid. By Dr. C. R. A. Wright.*

A solution of hydrobromic acid was prepared in the usual manner, by the action of sulphuretted hydrogen upon excess of bromine, in presence of water. It was carefully rectified over potassium bromide, and when submitted to analysis, was free from excess of bromine, sulphuric acid, and all other sulphur compounds.

* Chem. News, xxiii, 242.

The density was ascertained by weighing a known volume of the liquid; and the percentage of real acid subsequently determined, by titrating with a standard alkaline solution. Six analyses having been made of acid varying in specific gravity from 1·515 to 1·080, a mean curve of solubility was deduced, and the following table constructed.

Per centage of H Br.	Sp. gr. at 15° C.	Difference for 5 per cent.	Difference in 1 per cent.
nil	1·000	——	——
5	1·038	0·038	0·0076
10	1·077	0·039	0·0078
15	1·117	0·040	0·0080
20	1·159	0·042	0·0084
25	1·204	0·045	0·0090
30	1·252	0·048	0·0096
35	1·305	0·053	0·0106
40	1·365	0·060	0·0120
45	1·435	0·070	0·0140
50	1·515	0·080	0·0160

The author finds that the numbers given in the foregoing table, agree very fairly with similar determinations by other chemists: at the same time he feels compelled to take objection to the statements quoted in Watts's "Dictionary," Gmelin's "Handbook," and Brande's "Chemistry," on the authority of Löwig, that the specific gravity of the densest aqueous hydrobromic acid is 1·29; if this number be correct, the solubility curve, after passing the sp. gr. 1·5, must be abnormal; but it appears more probable, that the acid employed by Löwig was impure, and the relation between the density and percentage incorrectly assigned.

To set the question at rest, it is proposed to continue the subject, and to ascertain the specific gravity for higher percentages of hydrobromic acid.

J. W.

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*On the Reduction of Sulphuric Acid by Zinc Amalgam.** By J. Walz.

It has always proved a somewhat difficult problem, to effect directly the reduction of sulphuric acid to sulphuretted hydrogen, since in the majority of reactions in which a reduction takes place, it appears to be arrested at sulphurous acid, the more complete reduction to sulphuretted hydrogen having been observed only in a very few cases. The author, being cognizant of the above fact, was therefore surprised, when studying the action of sodium amalgam upon concentrated

* Chem. News, xxiii, 245.

sulphuric acid, to find that a considerable evolution of sulphuretted hydrogen took place; and pursuing the enquiry, he has succeeded in eliciting the fact, that if the sodium in the amalgam be replaced by zinc, not only may a very large quantity of sulphuretted hydrogen be formed, but that it is also possible to obtain, through a secondary reaction, an abundant deposit of sulphur in the free state. If a small quantity of sodium amalgam be covered in a test-tube with an equal amount of pure sulphuric acid, sp. gr. 1·84, the smell of sulphuretted hydrogen is at once perceived, and on pouring water into the test-tube, the solution appears milky from the suspension of finely divided sulphur. But, as might be anticipated, the action proceeds more regularly by employing an amalgam of zinc; in this case sulphuretted hydrogen is abundantly evolved, and at a certain period of the operation, sulphurous anhydride being simultaneously produced, the well known reaction takes place between them immediately, and free sulphur is deposited.

Towards the end of the operation, the reaction sometimes becomes unmanageable; if too much sulphuric acid be employed, mercury and sulphur are volatilized, and the liquid forced out of the flask; on the other hand, if it be successfully conducted, the generating flask should contain no oil of vitriol, but only metallic mercury, and anhydrous sulphate of zinc. No mercury enters into solution during the reaction.

The author criticises the observations of Messrs. Calvert and Johnson, published in 1866, upon the action of zinc upon the various hydrates of sulphuric acid at a high temperature, in which they state that the 4th, 5th, and 6th hydrates are acted upon with a preponderating evolution of sulphuretted hydrogen; but that if the sulphuric acid be diluted with more than six equivalents of water, pure hydrogen alone is formed. According to his own experience, the former reaction certainly did not occur, and Kolbe has disproved the latter, having shown that when chemically pure dilute sulphuric acid is acted upon by chemically pure zinc, a trace of sulphuretted hydrogen is always formed.

J. W.

Further additions to the history of Hydrate of Carbon Bisulphide.
By M. Ballo.*

In answer to Wartha's objection that the temperature, −11·5°, produced by directing a current of air on the surface of carbon-bisulphide covered with a layer of absolute alcohol, was too high for the existence of the solid bisulphide, that substance melting at from −12° to −13°; Ballo

* Deut. Chem. Ges. Ber., iv, 294.

states that he did not observe any formation of the solid substance, even when the temperature of the above liquid was lowered to $-18°$; this can be effected by cooling the bisulphide and alcohol with a mixture of ice and salt, and at the same time directing the air-blast on the liquid. If a layer of water be substituted for the alcohol, the formation of the hydrate of carbon bisulphide takes place at a temperature much higher than $-18°$. By directing a current of dry air on to the surface of carbon-bisulphide, Ballo found that solidification commenced at about $-7°$.

By passing air saturated with vapour of carbon bisulphide through a tube cooled by a freezing mixture to -15, the crystalline compound was produced; no crystals were obtained, however, when air dried by calcium chloride was employed.

Ballo remarks that the solid substance, obtained by Wartha by the sudden evaporation of a mixture of carbon bisulphide and ether by means of the air-pump, has not been shown to be free from water, which might also be solidified, he thinks, under the conditions employed.

W. H. D.

On Sulphuryl Chlorides. By A. Michaelis.*

The author holds that the statements of Williamson, Schiff, and Odling, with reference to the production of sulphuryl chloride, SO_2Cl_2, by the action of phosphoric chloride upon sulphuric anhydride, or on sulphuryl-hydroxyl-chloride SO_2,HO,Cl (Williamson, *Ann. Chem. Pharm.* xcii., 343; Schiff, *ibid.* cii, 114); and by the action of phosphoric oxychloride on lead sulphate (Odling, *Manual*, i, 162) are erroneous.

The action of phosphoric chloride on sulphuric anhydride perfectly free from hydrate, is sluggish and requires to be assisted by gentle warmth, the anhydride dissolves so soon as half the proportion of phosphoric chloride, indicated by the equation, $SO_3 + PCl_5 = SO_2Cl_2 + PCl_3O$ has been added, the excess causing evolution of chlorine and sulphur dioxide. By fractional distillation, a colourless oily liquid, boiling at 146° (corr.), of sp. gr. 1·819 at 18°, and composition $S_2O_5Cl_2$, was separated and named *pyro-sulphuryl chloride*. It dissolves slowly and quietly in water: in contact with phosphoric chloride it decomposes entirely into chlorine and sulphur dioxide. The author's numbers are almost identical with those of H. Rose.

The same substance is also produced by treating sulphuryl-hydroxyl-chloride with half the quantity of phosphoric chloride recommended by Williamson; if the whole proportion be employed, chlorine and sulphur dioxide are formed.

* Zeitschr. f. Chem. [2], vii, 149, from Jenaische. Zeitschr. vi, 235, 292.

Pyrosulphuryl chloride is also formed when four equivalents of sulphuric anhydride are heated for a long time to 160° with two equivalents of phosphorus oxychoride in a sealed tube.

Odling's statement that sulphuryl chloride is formed by the action of phosphorus oxychloride on lead sulphate is unintelligible to the author, who failed in detecting a trace of reaction between the two substances when they were heated together in a retort. The author concludes that sulphuryl chloride cannot be obtained from sulphuric anhydride, which acts rather as S_2O_6.

Sulphuryl-hydroxyl Chloride. By causing phosphoric chloride to react with sulphuric hydrate and fractionating the product, two liquids are obtained, namely pyrosulphuryl chloride boiling at 143° resulting from the action of phosphoric chloride on sulphuryl-hydroxyl chloride, and the last mentioned colourless compound, boiling at 158·4° (corr.), sp. gr. 1·776 at 18°. This substance resembles sulphuric anhydride in combining with explosive violence with water, decomposing immediately into sulphuric and hydrochloric acids. It may be conveniently prepared according to the equation $SO_4H_2 + 2POCl_3 = SO_3HCl + 2PO_3H + HCl$. The reaction $3SOH_2 + 2PCl_3 = 2SO_2 + SO_3HCl + 5HCl + P_2O_5$ takes place slowly in the cold, but energetically on heating the mixed substances.

On repeating an experiment of Carius (*Ann Ch. Pharm.* cvi, 307) by heating 70 pts. PCl_5 with 58 pts. $PbSO_4$ for 5 hours, the evolution of chlorine and sulphur dioxide ceased, and the dry mass became liquid. A small portion of the liquid distilled over at 80°—95° and consisted chiefly of thionyl chloride with perhaps a trace of sulphuryl chloride; a fraction boiling at about 110° was phosphorus oxychloride; the remainder, which was smaller even than the first portion, boiled at 145°—150° and was pyrosulphuryl chloride. The author concludes that this is not, as stated by Carius, a convenient method of preparing sulphuryl chloride, problematical traces only of that substance being found. The reaction is probably: $2SO_4Pb + 3PCl_5 = S_2O_5Cl_2 + 3POCl_3 + 2PbCl_2$ the second member of which equation is resolved by phosphoric chloride into chlorine, sulphur dioxide, and phosphorus oxychloride, the thionyl chloride resulting from the action of sulphur dioxide on phosphoric chloride.

The author prepared sulphuryl chloride by the method of Regnault (*Ann. Ch. Phys.* [3], lxxi, 445), and found that with a small quantity of water it forms sulphuryl oxychloride, which is also produced by heating it with sulphuric acid; with phosphoric chloride it decomposes into sulphur dioxide and chlorine.

F. H. H.

On the Action of Phosphorous Chloride on Anhydrides and Chlorides.
By Dr. A. MICHAELIS.*

Phosphorous Chloride and Thionyl Chloride. The reaction, $3\ PCl_3 + SOCl_2 = PCl_5 + POCl_3 + PSCl_3$ takes place slowly but completely when the reagents are heated together in sealed tubes to 160°. If an excess of thionyl chloride be employed, the phosphoric chloride separates in beautiful large transparent crystals.

Phosphorous Chloride and Sulphur Chloride (SCl). The reaction $3PCl_3 + 2SCl = 2PCl_3S + PCl_5$ is more rapid than that above mentioned. This is a convenient method of preparing phosphorus sulphochloride.

Phosphorous Chloride and Sulphur Dioxide. There seems to be no reaction either at 15° or 140°.

Phosphorous Chloride and Sulphuric Anhydride. The reaction $SO_3 + PCl_3 = SO_2 + PCl_3\ O$ between the cooled reagents is energetic and very simple; 40 p. chloride gave 43 p. oxychloride.

Phosphorous Chloride and Arsenious Oxide. The reaction $5\ As_2O_3 + 6PCl_3 = 4As + 3P_2O_5 + 6AsCl_3$, takes place directly, without the intermediate formation of phosphorus oxychloride: for this substance has no action on arsenic di-oxide even at 160°.

Phosphorous Chloride and Arsenic Oxide appear not to react even at 200°

F. H. H.

On the existence of the (so-called) Compound Ammonium Amalgams.
By the late C. H. WETHERILL.†

WURTZ did not succeed in forming a compound analogous to ammonium amalgam by using methylammonium chloride; but the author obtained the so-called amalgam of methylammonium when engaged in a series of experiments (described in Sill. Am. J. II, xl) by which it was demonstrated that ammonium amalgam is merely a metallic froth. The salt used was the oxalate of methyl ammonium, and the amalgam (froth) obtained was of essentially the character as ammonium amalgam, but less turgescent. But H. Landolt having stated "that the turgescence of the mercury takes place only when the preparation contains ammonium chloride," it became necessary to repeat the experiments. This was done with the result of confirming the author's former statements. The methylammonium oxalate was prepared by Carey Lea's process, and its purity insured by recrystallisation from alcohol and ether.

C. H. G.

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* Zeitschr. f. Chem. [2], vii, 151, from Jenaische Zeitschr. vi, 240.

† Sill. Am. J. [3], i, 369.

On some Reactions of Water-Glass. By F. A. Flückiger.*

It was pointed out long ago by Vogel that silica is thrown down on mixing strong solutions of potassium silicate and potassium borate containing excess of alkali. The author, after numerous experiments, has arrived at the conclusion that all the most easily soluble salts of potassium, sodium, lithium, and ammonium possess the property of precipitating silica from strong solutions of water-glass. This property is exhibited, for example, by cold saturated solutions of ammonium chloride, bromide, sulphide, phosphate, molybdate, nitrate, and acetate; sodium chloride, nitrate, nitrite, and arsenate; potassium iodide, sulphide, sulphocyanate, tartrate, and acetate; lithium nitrate, sulphate, and acetate; and many other salts. Most of these salts lose the property when their solutions are diluted, but several of the ammonium-salts retain it even after being largely diluted. When, for instance, a solution of sodium silicate of sp. gr. 1·392 is diluted with 29 parts of water, and a few drops of solution of ammonium chloride (1 in 8 of water) are added, deposition of silica takes place on warming, although the solution contains only 2 per cent. of silicate. A solution containing 0·5 per cent. of silicate exhibits only a slight turbidity after some time on addition of ammonium chloride, but is precipitated at once by potassium sulphocyanate or ammonium nitrate. Methylamine and ethylamine hydrochlorides are much less active. Cold saturated solution of potassium bromide or chloride decomposes the silicate on warming, but not at the ordinary temperature. Cold water saturated with crystallised sodium sulphate produces no precipitate even on warming; but when the salt is dissolved in such a quantity of hot water that the solution contains 1 part of anhydrous sulphate to 2 parts of water, a solution of sodium silicate of the strength mentioned above, heated to the same temperature, is precipitated by it. Potassium and sodium tartrate, potassium nitrate, ferrocyanide, and ferricyanide are too sparingly soluble in water to decompose sodium silicate of the strength given.

The behaviour of sodium nitrate is remarkable. The author employed a solution of sodium silicate of sp. gr. 1·392, containing so little excess of alkali that the first drop of alcohol or any free acid produced a precipitate of silica. On mixing this solution with a solution of sodium nitrate in 1 part of water, silica is at once thrown down; but when a solution of the nitrate in 2 parts of water is mixed with the silicate, volume for volume, no precipitate is produced. On heating the mixture to 54°, however, gelatinous silica separates and the whole becomes nearly solid. If now the flask containing the jelly be suddenly cooled to the ordinary temperature, or to 0°, the jelly is redissolved as rapidly as it was formed. This experiment may be repeated

* Zeitschr. f. Chem. [2], vii, 89, from N. Repert. Pharm., xix, 257.

any number of times, and is exceedingly well adapted for a lecture-experiment. Dissolution of the precipitated silica takes more slowly when the quantity of nitrate is increased, and ceases altogether when 2 parts of the nitrate solution are employed to 1 part of silicate. When, on the other hand, 1 part of the nitrate is added to 2 or 3 parts of silicate, only a scanty precipitate is produced, even at 100°.

Solution of ammonia of sp. gr. 0·921 produces an abundant precipitate of gelatinous silica in solutions of sodium silicate of sp. gr. 1·392. The precipitate dissolves on warming and re-appears as the solution cools.

Sodium silicate is decomposed also by propylamine, but not by conine or nicotine. A drop of bromine or a bubble of chlorine produces an immediate precipitate of silica: iodine does not affect the solution. But this property of decomposing silicates is possessed in the highest degree by creosote from beech-wood and by carbolic acid. Pure chloral hydrate also decomposes sodium silicate. Dilute solutions of albumin and gelatin throw down silica; almond-emulsion does not. Gum arabic, as has long been known, decomposes sodium silicate. The precipitate consists chiefly of silica, and contains no gum: its formation is due to the salts of the gum. Strong solutions of sugar, dextrin, glycerin, and urea produce no precipitate even on warming.

J. R.

On Flückiger's Water-glass Reactions. By W. Heintz.*

Flückiger described some interesting reactions of water-glass in vol. 144 of the *Arch. Pharm.*, from which he drew the conclusion that the most soluble salts of potassium, sodium, lithium, and ammonium possess the power to throw down silicic acid from a concentrated water-glass solution; or, at any rate, if the precipitate were not pure silica, that it only contained more or less of the base carried down in a loose state of combination.

As there is no conceivable action between neutral salts of the fixed alkalies and water-glass, through which free silicic acid would become separated, it appeared much more probable that these neutral salts would behave to a solution of water-glass as they do to one of soap, *i.e.*, they would precipitate, not silicic acid, but an alkaline silicate. Experiment has confirmed this supposition.

A concentrated solution of soda water-glass was precipitated by concentrated ammonia water, and the precipitate thoroughly washed with the same liquid by help of the water air-pump, and silica and soda estimated in the still moist mass:

* Arch. Pharm. [2], cxlvi, 1.

	Found.	Calculated.	
Silicic acid	79·38	79·47	$4SiO_2$
Soda	20·62	20·53	$1Na_2O$

therefore the precipitate is unaltered water-glass.

Again, a solution of water-glass was precipitated by a concentrated solution of sodium nitrate, the precipitate first washed, as before, with the same solution, and lastly, with dilute alcohol. On analysis, it was shown that the precipitate consisted of unaltered water-glass. The precipitation by ammonia may be utilized in preparing chemically pure water-glass.

C. H. G.

On the Cerite Metals. By KARL ERK.*

IN the course of his paper the author refers to the following authorities:—Mosander, *Pogg. Ann.* xlvi, 548; xlvii, 207; lvi, 504; Bunsen, *Ann. Ch. Pharm.*, cv, 40; Jegel and Vogler, *J. pr. Chem.*, lxxiii, 200; Hermann, *ibid.*, lxxxii, 385; xcii, 113; Lange, *ibid.*, lxxxii., 129; Czudnowicz, *ibid.*, lxxx, 16; lxxxii, 277; Holzmann, *ibid.*, lxxv, 321; lxxxiv, 76; Rammelsberg, *ibid.*, lxxvii, 67; *Pogg. Ann.*, cviii., 40 and 435; Marignac, *Ann. Ch. Pharm.*, viii, 265; xxvii, 209; Beringer, *ibid.*, lxviii, 212; Popp, *ibid.*, 131; Zschiesche, *J. pr. Chem.*, civ. 174; cvii, 2.

Separation of Cerium from Lanthanum and Didymium.—The author prepared pure cerium oxide in the following manner. Finely powdered cerite was made into a thin paste with sulphuric acid, kept warm for several hours, and then gently heated; the white powder was then exhausted by repeated treatment with boiling dilute nitric acid; the filtered solution, after treatment with sulphydric acid, and filtration, was mixed with a little hydrochloric acid and oxalic acid; the oxalates were ignited in a platinum dish, with constant stirring, and dissolved in rather strong nitric acid; the solution was evaporated to a syrupy consistence, and then mixed with a large quantity of boiling dilute sulphuric acid; and the precipitate of basic ceroso-ceric sulphate was washed with hot water as long as the washings gave a precipitate with oxalic acid.

The addition of magnesia to the oxalates previous to ignition, as recommended by Bunsen and Jegel, is unnecessary; it is also very difficult to separate the magnesia perfectly from the ignited product.

Popp's method, which consists in treating a solution containing cerium, lanthanum, and didynium with chlorine and sodium acetate, is efficient for the preparation of pure cerium salts, but not for the preparation of pure lanthanum and didynium compounds, on account of

* Zeitschr. f. Chem. [2], vii, 101—115.

the easy reducibility of the ceroso-ceric hydrate by free acetic acid. The author also observes that the precipitate described by Popp as cerium peroxide is in reality a basic acetate.

Separation of Lanthanum and Didymium.—The solution containing both metals was precipitated to the extent of one half with ammonia; the precipitate collected, washed, and digested for one day with the mother liquor at the ordinary temperature; and the filtrate was again treated in the same way. After the second treatment, it gave but slight indication with the spectroscope of the absorption bands of didymium; after four such fractional precipitations the didymium lines were no longer visible in 30 centimetres of solution. The didymium solution was considered to be free from lanthanum when no difference in colour or composition could be found between a fractional precipitate and the precipitate obtained from the filtrate.

The analyses of the sulphates gave the atomic weights La = 90·34 – 90·18; Di = 94·9 – 94·86 – 95·64. Zschiesche found for

Lanthanum (mean of 6 determinations) 90·18
Didymium („ 5 „) 93·0 –96·16.

The author confirms generally, the description given by Bunsen and Bahr of the didymium absorption spectrum.

Separation of Yttrium from Lanthanum and Didymium.—The author did not succeed in preparing pure yttrium salts, but found that in the separation of didymium by fractional precipitation, the yttrium oxide occurs in largest quantity in the extreme precipitates of didymium oxide, from which it may be tolerably well separated by dissolving in nitric acid and boiling with sodium sulphate, the double sulphate formed with yttrium being much much more soluble than the didymium salt. The author found, contrary to Popp's statement, that yttrium solutions have no characteristic absorption spectrum.

Composition of Cerium Oxides. Ceroso-ceric Oxide.—The oxides obtained in various ways were converted into ceroso-ceric sulphate by treatment with concentrated sulphuric acid, and the ceroso-ceric sulphate was converted, by ignition until the weight was constant, into ceric sulphate from which the percentage of cerium was deduced. Seven determinations made with oxides prepared by igniting ceroso-ceric hydrate, ceric nitrate and ceric oxalate gave a mean Ce = 88·99; Ce_2O_4 requires Ce 81·18; Ce_2O_3 requires Ce 79·31.

The author could not, either by heating ceric oxide in oxygen or by igniting ceric nitrate, obtain a cerium peroxide, such as Rammelsberg described as $Ce_{12}O_{17}$.

Ceroso-ceric hydrate, prepared by boiling ceroso-ceric sulphate with ammonia, and drying over lime and sulphuric acid gave 15·1 per cent. H_2O, corresponding with Rammelsberg's formula $Ce_3O_4.3H_2O$, requiring 13·7 per cent. H_2O.

Ceric oxalate, air dried, contains $4H_2O$; dried at 100° it contains H_2O, corresponding exactly with didymium oxalate.

Ceroso-ceric sulphate, air dried, contains $S_4O_{16}Ce_3 + 14\ H_2O = (SO_4)_4\ Ce'''_2Ce'' + 14H_2O$.

Basic ceroso-ceric sulphate, dried over sulphuric acid contains $SO_6\ HCe_2 + 2H_2O$. By repeated boiling with water nearly all the sulphuric acid may be removed.

Basic ceroso-ceric nitrate.—When a concentrated solution of ceroso-ceric nitrate is poured into a large quantity of hot dilute nitric acid, a yellowish white flocculent precipitate, soluble in pure water, is formed, which when dried at 110° contains NO_8HCe_4.

Basic ceroso-ceric acetate becomes less soluble by drying; dried over sulphuric acid it contains $C_4H_7Ce_5O_{10}$.

The *electrolysis* of fused cerium chloride, prepared similarly to magnesium chloride, gave a small quantity of metallic cerium as a grey-black powder, and at the same electrode reddish-white scales of cerium oxychloride identical with the substance found by Wöhler in preparing cerium. A large quantity of Ce_3O_4 was formed during the operation, as the result of fusing cerium chloride in presence of air and moisture. By the electrolysis of acid or neutral solutions of ceric sulphate, a basic sulphate of the composition $SO_6HCe_2 + 2H_2O$, and therefore identical with the product of other known reactions, is formed. By electrolysis of solution of cerium nitrate sufficient ammonia is formed to completely precipitate the whole of the cerium oxide. An aqueous solution of basic cerium acetate gave by electrolysis a basic acetate, which, on drying, appeared as a brownish red amorphous substance.

F. H. H.

On the Formation of Diammonio-zinc Chloride in Leclanché's Manganese-Elements. By L. Priwoznik.*

In the jars of Leclanché's manganese-elements, after they had been in use for several days, there was found a deposit of crystals, identical in form and composition with the diammonio-zinc chloride, $ZnCl_2(H_3N)_2$, which Marignac had previously obtained by adding ammonia to a solution of zinc chloride until the precipitate first formed is redissolved, and allowing the solution to evaporate spontaneously. The chemical process in the cell is represented by the equation

$$2H_4NCl + Zn + 2MnO_2 = 2H_3N + ZnCl_2 + Mn_2O_3 + H_2O,$$

in accordance with the observation, that the manganese dioxide loses its efficiency in consequence of undergoing a reduction. The formation of the crystals, which causes a speedy diminution of the strength of

* Pogg. Ann., cxlii, 467.

the current, may be prevented by repeated addition of hydrochloric acid until the free ammonia is neutralised.

R. S.

Researches on Ferric Hydrate. By E. BRESCIUS.*

FERRIC oxyhydrate was precipitated by ammonia from a solution of ferric chloride, fully washed by decantation, pressed, and dried at ordinary temperatures. The drying of the precipitate was attended with some difficulty, since, when nearly dry, ferric hydrate has almost as great a tendency to take up water as oil of vitriol itself. The experiments were carried out in the following manner:—In each case, about 0·5 grm. of the apparently dry hydrate was taken, ground as fine as possible, placed over oil of vitriol, and weighed at intervals of eight to fourteen days till no further loss occurred; this generally required about three months. The weighed portion was heated in a water-bath till no more water was given off even in forty-eight hours, and was then ignited.

In the first experiment the total combined water was found to be 10·598 parts, for 80 parts (1 atom†) of ferric oxide.

Second experiment—in two estimations the hydrate lost on 80 parts oxide

At 100° C	4·705 and 4·87 mean	4·7875
Ignited	6·168 and 6·012 „	6·0900
	Total.....	10·8775

Attention is called to the change which ferric hydrate undergoes by standing, even under water, a change which is rendered evident by the less ready manner in which it dissolves in dilute acids, and which appears to increase in amount with the time during which the experiment is carried out. To remove this source of difficulty or to reduce it to a minimum, by shortening the time during which the original precipitate remains in contact with water, the author first added so much absolute alcohol to the fully washed precipitate, that ether would mix completely with the latter, which was then rendered free from adhering moisture by washing with that very volatile liquid. By subsequently drying the so-prepared mass over oil of vitriol, ferric hydrate was obtained as an impalpable powder instead of as a horny mass.

Third experiment—with ether-dried hydrate which had been kept over oil of vitriol till no further loss of weight took place—two determinations reckoned on 80 parts oxide:

* J. pr. Chem. [2], iii, 272—285.

† Fe = 28 O = 8.

At 100° C	9·189 and	9·301	mean	9·245
By ignition.....	10·270 and	10·263	„	10·266
				19·5115

Fourth experiment—with ether-dried hydrate—reckoned as before on 80 parts oxide:

At 100° C.....	9·152
By ignition	9·261
	18·413

Fifth experiment, similar to last:

At 100° C	7·950 and	8·068	mean	8·009
By ignition	8·149 and	7·841	„	7·995
				16·004

These experiments lead to no definite formula for ferric hydrate.

C. H. G.

On Brittle Silver. By A. H. Church, M.A.*

Some curious silver ornaments, bearing unmistakeable evidence of great antiquity, and possessing moreover, a remarkable physical structure, have been found, together with other specimens of antique art, in several tombs recently opened near the site of the ancient city of Idalium, in the island of Cyprus. Their age is calculated to be not less than 1,500 years, and owing to their lengthened entombment, they have become covered externally with a friable, sub-metallic crust, to the depth of about $\frac{1}{30}$th of an inch, which crust proved upon analysis, to be composed principally of finely divided silver, mixed with the chloride and sulphide of that metal, and a little basic carbonate of copper.

Beneath this layer, the substance appeared white, metallic, and uniform, but was remarkable for its extreme brittleness, the object being easily snapped in numerous pieces by a very slight pressure. Towards the thicker portion of the ornament (which was shaped in the form of a crescent), there existed a kind of core, similar in colour to the main mass of the object, but possessing great tenacity and ductility, and capable of being wrenched out of the surrounding brittle mass. The results of the analyses, both of the crystalline, brittle silver, and of the central ductile portion, were precisely identical, both were found to contain in 100 parts,

* Chem. News. xxiii, 243.

	Per cent.
Silver	94·69
Gold	0·41
Copper	3·43
Lead	0·28
Antimony, with trace of arsenic and bismuth	1·21
	100·02

It was also ascertained, that by gentle hammering or rolling, the brittle mass could be easily restored to its pristine malleable condition, while its density gradually rose from 9·06 to 10·2. It was therefore, a molecular, and not a chemical change which had taken place. Some unknown agency, aided by the lapse of centuries, had affected the external portions of the silver, and induced a cryptocrystalline structure in what had previously been a homogeneous alloy.

An analysis by the late Mr. Warington of a Romano-British silver urn, in which a similar structure had been induced, directly confirms the foregoing results. He agrees also with the author in his interpretation of the experimental results, attributing the brittleness of the silver to molecular disturbance, and not in any way whatever to chemical change.

J. W.

On the Reduction of Silver Chloride in the Wet Way. By Dr. Geager.*

The silver chloride is dissolved in ammonia; the solution put into a stoppered bottle; and zinc, in moderately sized pieces, is gradually added until all the silver is reduced. The precipitate is washed by decantation till free from ammonia, and then poured through a funnel into a second bottle. The funnel is partly filled with pieces of glass, so as to allow the fine precipitate of silver to pass, but to retain the larger-sized pieces of zinc. The precipitate is now repeatedly treated with strong hydrochloric acid, and, if necessary, even boiled with it, until the dark grey colour is changed into white. The silver is now again washed with distilled water, treated with ammonia, to remove traces of silver chloride formed, and, finally once more washed, first by decantation and lastly on a filter. The silver so obtained is perfectly pure. An ammoniacal solution of silver nitrate may be treated in the same way; and even if it contains copper, as obtained by the solution of silver coins, for example, pure silver will be obtained, provided the quantity of zinc employed is insufficient to precipitate all the silver present.

A. D.

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* Dingl. Polyt. Journ., ce, 105.

Recovery of Silver Nitrate from the Silver Bath. By DR. GRAGER.*

THESE solutions generally contain, besides the silver, salts of ammonium, cadmium, zinc, iron, and copper. To separate these metals, the solution is boiled for some time with freshly precipitated pure silver oxide; the clear filtered solution is evaporated to dryness, and the residue is fused to expel ammonium salts, when pure nitrate of silver is left. The precipitate which contains the excess of silver oxide used, is best kept in the moist state, and may be employed in a second operation in place of fresh oxide, until all the oxide of silver contained in it is dissolved.

A. D.

Mineralogical Chemistry.

On the Molybdates and Vanadates of Lead, and on a New Mineral from Leadhills. By A. SCHRAUF.†

Eosite.—THE author describes a specimen of "vanadio-molybdate of lead" from Leadhills, which differs so strikingly in its crystallographic and chemical characters from its nearest allies, wulfenite and descloïzite, that he regards it as a type of a new species, and on account of its aurora-red colour, gives it the above name. Its matrix, abundantly beset with crystals of cerussite, is cellular ochreous galena. The cerussite is in several points encrusted with moss-like aggregations of delicate, minute, acicular, yellow crystals of pyromorphite, which often completely cover in the small red octohedrons of eosite attached to the cerussite below. The measurements of the yellow crystals proved them to be regular hexagonal prisms, and an examination of the small amount of material at disposal showed that it contained no vanadium. The crystals of eosite are below ½ millim. in size, and though readily detached from the cerussite, are only with difficulty freed from the pyromorphite; their hardness lies between 3 and 4, and, when crushed, they show slight traces of cleavage.

The red of eosite is deeper than that of chromate of lead, and approaches that of realgar; in powder it is brownish orange, somewhat darker than that of red chromate of lead.

Eosite, when pulverized, becomes white in contact with hydrochloric acid, chloride of lead being formed. The yellow solution,

* Dingl. Polyt. J., cc, 109.

† Proc. Royal Soc., 1871, 451.

evaporated to dryness with alcohol, gives a bluish residue, verging on greenish grey. Wulfenite, treated in the same manner, gives a deep blue deposit, vanadinite a yellowish or bluish green one, and crocoite a feeble yellowish green one. Eosite heated in a tube, darkens, and, when cold, regains its original colour. Fused with bisulphate of potash, it forms a transparent, nearly colourless mass, which as it cools becomes for a moment reddish brown, and finally assumes a light orange-brown tint. Similar changes of colour were noticed on fusing a mixture of two or three parts of molybdate and one of vanadate of lead with the same reagent. When the aqueous solution of the eosite which had been fused with bisulphate was boiled with tin-foil, it assumed a faint greenish blue tint, and, in a second experiment, gave on evaporation a yellowish brown residuum, possibly due to vanadium. These reactions prove the mineral to be essentially a vanado-molybdate of lead, the molybdenum probably being in excess. It has still to be proved that the chemical reactions of vanadate and molybdate of lead are essentially different from those of eosite, and that this mineral cannot be identified with the red wulfenites already known, or with the crystals of dechenite vanadinite or descloizite.

The eosite crystals present simple octoïd forms, one of them alone showing the plane (001). The measurements of three crystals gave the mean results :—

$$c\ ,\ p = (001), (111) = 65^\circ\ 50'$$
$$p\ ,\ {}'p = (111), (\bar{1}11) = 77^\circ\ 50^\circ,$$

and consequently,

$$(111)\ ,\ (101) = 38^\circ\ 55' \qquad (111)\ ,\ (100) = 51^\circ\ 5'$$
$$(111)\ ,\ (110) = 27^\circ\ 10' \qquad (100)\ ,\ (110) = 45^\circ\ 5'.$$

These data give the parametral proportion, $a : b : c = 1{\cdot}003 : 1 : 1{\cdot}375$. Eosite, in short, belongs to the pyramidal system with the axial proportion :—

$$a : a : c = 1 : 1 : 1{\cdot}3758; \qquad (001), (111) = 62^\circ\ 50',$$

and unites the crystallographic system and lateral angles of wulfenite with the pyramidal angle of descloizite.

Chemical Properties of the Chromo-wulfenites.—H. Rose found chromium in the red wulfenites of Rézbánya (Banat) and Siberia. On a specimen of pyromorphite from Ruskberg (Banat) the author found deep red octohedrons of wulfenite, 1—2 mm. in size, those from Phenixville being twice as large. The red of eosite is deeper than that of crocoite, more intense than that of the Ruskberg cromo-wulfenite, and less mixed with yellow than in the Phenixville mineral. The streak of eosite is browner than that of crocoite, and those of the

Ruskberg and Berezowsk crystals are identical. The Ruskberg and Phenixville chromo-wulfenites, when treated with hydrochloric acid, give deep blue precipitates, with a yellowish green margin; by fusion with bisulphate, they become faintly yellowish green when cold, the Phenixville specimens in particular exhibiting a brownish purple tint when first fused. This mineral, then, like the red wulfenites of the Banat, contains chromium, and according to Mr. Smith, vanadium also. Wöhler found the latter metal in *genuine* wulfenites.

Chemical Properties of Dechenite, Descloïzite, and Vanadinite.—Eosite, as containing vanadium, stands next to these vanadates of lead. The author was, through lack of material, unable to examine descloïzite, but investigated two specimens of vanadinite from Kappel, in Carinthia, and one of dechenite. Variety A of the Kappel mineral consisted of dark greenish brown crystals, resembling in all external characters Peruvian descloïzite. Variety B of vanadinite has a light carnation tint and faint vitreous brightness, which is soon lost in moist air, the moisture of the breath producing a superficial decomposition. The author failed to detect the presence of arsenic in this mineral. Experiment gave evidence of a notable difference between eosite, descloizite, and vanadinite, and of the nearly absolute identity of the two varieties of Kappel vanadinite, variety A resembling Peruvian descloïzite, while variety B bears some resemblance to Schlettenbach dechenite. The latter mineral is likewise of a carnation colour and easily affected by moisture, a globular yellowish grey effervescence being produced. The analogy applies also to their chemical composition, in that they both contain a notable amount of zinc. It seems probable that in variety A also there is a small proportion of this metal.

Crystallographic Forms of Descloizite and Vanadinite.—The similarity of the pyramidal angles of eosite and Peruvian descloïzite led the author to expect the existence of similar forms in the B variety of vanadinite or in dechenite. On dechenite only an occasional angle of about 90° could be determined. The measurements of angles on three crystals of the B variety of vanadinite accord perfectly with those formerly made by the author on the A variety, and with those of Des Cloizeaux on Peruvian descloïzite. The author further asserts an isormorphism between the latter mineral and anglesite, and, in classing descloïzite with monovanadates, calls in question the correctness of the formula assigned to it by Damour.

Crystallographic Form of the Chromo-wulfenites.—On the assumption that changes might arise in the angles of wulfenite by the introduction of chromium, the author measured the chromo-wulfenites of Ruskberg and Phenixville, and found, as G. Rose had previously done in the case of the Beresowsk variety, that the angles differ but slightly from

those generally accepted. His results confirmed the fact that the characteristic forms of eosite are wanting in the red wulfenites.

W. F.

A Second Instance of Metamorphism in Meteorites. By S. MEUNIER.*

THE author having previously shown† that the meteoric rock, tadjerite, represents the metamorphic form of a totally different rock, aumalite, now recognizes in stauropolite, the rock composing the meteorite which fell on the 24th March, 1857, at Stauropol in the Caucasus, the product of the metamorphism of a rock, not analogous in appearance, termed montrejite.

Though these two rocks appear at first sight to differ greatly, montrejite being ashen-grey and very friable, and stauropolite having a blackish hue and considerable toughness, still, on nearer examination they show a striking resemblance. Their structure is identical; in both we have chondra enclosed in a stony mass; both contain small grains of nickeliferous iron, not unfrequently disposed on the periphery of these chondra. Their densities differ but slightly; the mean of the determinations of that of stauropolite is 3·59, in the case of montréjite it is 3·54. And, as seen below, they have nearly the same chemical and minerological composition:—

	Nickeliferous Iron.	Magnetic Pyrites.	Peridot.	Undecomposed Silicates.	Chromite.	
Montrejite	11·60	3·74	44·83	38·00	1·83	100·00
Stauropolite	10·25	2·95	45·65	41·17	—	100·02

Nothing is more easy than the conversion of the former into the latter, to give montrejite the physical characteristics, as regards colour and cohesion, of stavropolite. It suffices to submit it to the operation used for changing aumalite into tadjerite, to heat it for a few minutes in absence of air in a crucible over a coke fire.

The author is more than ever of opinion that the simple method of

* Compt. rendus, lxxii, 452. † Compt. rendus, lxxi, 771.

calcination will facilitate the study of the mineralogical character of meteorites. The chondra of the Montréjeau stone appear all of one kind, and they are held to have the same composition. Heat, however, stamps them with diverse characters, and enables us to recognize several different species among them.

W. F.

Further Inquiry into the Metamorphism of Meteorites. By S. MEUNIER.*

IT has already been noticed that at a suitable temperature the two grey rocks of which the meteorites of Aumale and Montréjeau are types, are converted into black varieties, represented by the falls of Tadjéra and Stauropol respectively. It is now found that for the change to be complete, the bright red heat of a good coke fire is required. At a less elevated temperature, products are formed which differ altogether from those just mentioned, but are worthy of study. Montrejite, for instance, after being heated with a gas flame, in no way resembles stauropolite, the mass of the stone being still grey and friable; the chondra enclosed in it are, however, quite black. This product of imperfect calcination corresponds in all its characters with a number of meteorites composed of a rock that the author, in his "Etablissement des Types de Roches Météorites," has termed belajite.† The falls referred to are those at Bjelaja Zerkow, Kiew, on the 4th January, 1797; at Slobodka, Smolensk, on the 10th August, 1818; and at Macayo, Brazil, on the 11th November, 1836. Allied to this rock is that bearing the name butsurite, which differs from belajite only in the lesser magnitude of its chondra. Butsurite is represented by the falls of Gross-Diwina, Hungary, on the 24th July, 1837, and that near Butsura, in India, on the 12th May, 1861.

Belajite and butsurite, then, constitute two new metamorphic types derived from montrejite, as stauropolite has been, but representing, in respect of the temperature to which they have been subjected, a state of condition intermediate between the last two rocks.

The fact of the chondra of montrejite undergoing metamorphosis before the mass cementing them together, confirms the author's view that the black matter is formed at the expense of the pyroxenic minerals present, since they are more abundant in the spherules than in the cement.

W. F.

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* Comptes rendus, lxxii, 508. † Cosmos, February 5th, 1870.

Conversion of Serpentine into Tadjerite. By S. MEUNIER.*

SUCH terrestrial silicates as lherzolite and serpentine differ but little in composition from aumalite, chantonnite, luceite, montrejite, and other meteoric lithological types. Among the magnesian rocks are some whose structure is identical with that of some of the meteorites, and of them the serpentines are the most remarkable, being formed like the meteorites in question, of silicates enclosing in the same state of dissemination as the nickeliferous iron and troilite of meteorites, granules of magnetite and pyrites.

The difference in composition of serpentine and the meteoric rocks lies in the presence of water in the terrestrial body, and in an oxidized condition of certain of its elements. To convert the serpentine into tadjerite, then, it has to be simultaneously dehydrated and reduced. But as serpentine parts with all its water at a red heat only, and it has been shown that at this temperature magnesian meteorites undergo a material change, it is clear that by this operation we do not obtain a product corresponding to the grey meteorites, but we form artificially the cosmical metamorphic rock.

The author exposed a light green serpentine from Chambave, in the Valley of Aosta, to a red heat in a current of hydrogen. In a few minutes the rock loses water and takes a dark hue, which becomes more and more intense, and is in every respect like that of tadjerite. The black colour appears as soon as a red heat is reached. The change, however, is only superficial, unless a porcelain tube and a coke fire are employed.

The black product has all the appearance of tadjerite, and is softer than it, though considerably harder than the serpentine. The author believes tadjerite may have been subjected to pressure, and explains the looser structure of the artificial rock by the loss of some of its constituents. When chemically examined, it shows a perfect accordance in its properites with the material of the Tadjéra meteorite.

If coal gas be used in the place of hydrogen, fragments of some size can be completely transformed. In one experiment pieces of from 3 to 5 cubic centimetres, of a green serpentine from Impronneta, were heated for $1\frac{1}{2}$ hours. When washed from deposited carbon and broken the interior was found to be perfectly white, whilst the surface and a layer some millimetres thick were black. It is shown by this experiment that there is a stage in the transformation preceding the blackening, and that the latter appearance is not due to the reduction of the iron, for that of the colourless centre had also been reduced to metal, and precipitated chloride of copper.

W. F.

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* Compt. rendus, lxxii, 541.

Contributions to Mineralogy. By G. vom RATH.

(Pogg. Ann. Ergänzungsband, v., 321—444.)

ON the Crystalline System of Humite.—Occurrence of Monazite at Lake Laach.—Occurrence of Babingtonite at Herbarnseelbach.—On the Angles of Albite.—On the Angles of Montecellite.—The Scalenohedron R_4 observed on Crystals of Calcspar from Alsten Moor.

On the Water of the Irish Sea. By T. E. THORPE and E. H. MORTON.*

THE water was collected by Captain Temple in the immediate neighbourhood of the Bahama Bank Light-ship, 54° 21″ N. 4° 11′ W., seven English miles N.W. of Ramsay, Isle of Man. This position is about equidistant from the coasts of England, Ireland, and Scotland, and a strong current from the south, probably from the Atlantic Ocean, flows past the ship for the greater part of the day, so that the authors considered themselves entitled to assume that they were dealing with water of the Atlantic Ocean, which had been exposed in its passage through the Irish Channel to all the influences of the neighbouring coasts.

The authors received the water in the beginning of January, 1870. Its specific gravity compared with air-free distilled water was 1·02721 at 0°, and 1·02484 at 15°. Von Horner found the specific gravity of the Atlantic water 1·02875 at 0°. Schweitzer gives the specific gravity of the water off the Pas de Calais at 15·5° as 1·0271, and near the land as 1·0268.

1. *Total solid contents* dried at 180° (1″) 33·8360, (2″) 33·8411 mean 838·83855 grms. per thousand. The saline contents are therefore smaller than those of the North Atlantic, but larger than those of the North Sea.

Decomposition of the magnesium chloride was counteracted by the addition of a weighed quantity of sodium carbonate The methods employed in the remaining determinations call for no special comment.

The following table contains in grams per litre the collected results of the analysis :—

Chlorine	18·62650
Bromine	0·06133
Sulphuric acid (SO_4)	2·59280
Lime (total)	0·57512

* Ann. Chem. Pharm., clviii, 122—131.

Calcium carbonate	0·04754
Magnesia	2·03233
Alkaline chlorides	27·18363
Potassium	0·39131
Sodium	10·40200
Ferric oxide	0·00465
Ammonia	0·00011
Nitric acid	0·00156
Total solid contents	33·83855

If we arrange the foregoing constituents on the assumption that the strongest bases are combined with the strongest acids, we obtain the following table:—

Sodium chloride	26·43918
Potassium chloride	0·74619
Magnesium chloride	3·15083
Magnesium bromide	0·07052
Magnesium sulphate	2·06608
Magnesium carbonate	trace
Calcium sulphate	1·33158
Calcium carbonate	0·04754
Lithium chloride	trace
Ammonium chloride	0·00044
Magnesium nitrate	0·00207
Silica	trace
Ferrous carbonate	0·00503
Total by addition of constituents	33·85946
Total found directly	33·83855

The sample analysed as above was collected in winter; another sample collected in August in the same neighbourhood, yielded the following results:—

	Mean.
Total solid contents	34·0821
Sulphuric acid	2·6239
Chlorine	18·7353

From this it appears that the water of the Irish Sea contains somewhat more solid constituents in summer than in winter. The authors quote sundry analyses of various sea-waters for comparison with the above.

E. T. C.

Organic Chemistry.

On a new series of Aromatic Hydrocarbons. By TH. ZINKE.*

WHEN benzylic chloride and finely divided copper are heated together, hydrochloric acid is evolved, and cuprous chloride and a resinous hydrocarbon are formed. The formation of this resin can be avoided by diluting the benzylic chloride with a benzene hydrocarbon; a mixture of at least two different hydrocarbons is obtained, *the quantity of which is always larger than that of the benzylic chloride*, from which it follows that the benzene hydrocarbons take part in the reaction—certainly a most remarkable fact.

Zinc dust and reduced iron, which act like copper, have the advantage that the reaction takes place at a much lower temperature.

By using benzylic chloride, benzene and zinc dust, a product was obtained, the lower-boiling portion of which consisted of a solid hydrocarbon $C_{13}H_{12}$, which melts at 24°—25°. The distillate solidifies to a crystalline mass consisting of prismatic needles; on slowly cooling, large fine tables are sometimes formed. This body is readily soluble in concentrated nitric acid, a crystalline nitro-product being formed; it is only slowly oxidized by boiling with dilute sulphuric acid and potassium dichromate, the products consisting of a little benzoic acid and an isomeride of benzophenone which crystallises in fine monoclinic prisms, melting at 26°—26·5°.

From these oxidation products, as well as from the mode of formation of this hydrocarbon, it appears that its constitution is expressed by the formula $C_6H_5—C.H_2—C_6H_5$; it is *diphenylmethane*, and most probably identical with the diphenylated marsh-gas which Jena obtained by distilling barium diphenylacetate with soda-lime.†

Toluene and benzylic chloride yield the hydrocarbon $C_{14}H_{14}$, a colourless oil which boils at 277°, and gives with concentrated nitric acid a liquid nitro-compound. On boiling it with the oxidising mixture, a well characterised acid, $C_{14}H_{10}O_3$ is obtained, which combines with nascent hydrogen, forming the hydro-acid $C_{14}H_{12}O_3$ which is isomeric with benzilic acid.

This hydrocarbon has probably the constitution $C_6H_5—CH_2—C_6H_4—CH_3$; it is isomeric with dibenzyl and ditolyl.

It is very difficult to find an explanation for the reaction by which these hydrocarbons are formed; it does not take place between equal numbers of molecules, but requires an excess of benzylic chloride, the products being a small quantity of metallic chloride, and much hydrochloric acid,

* Deut. Chem. Ges. Ber., iv, 298.

† Ann. Chem. Pharm., clv, 86.

besides the new hydrocarbons. The author hopes that the examination of the products of higher boiling point will clear up this point.

C. S.

Preliminary Notice on a Crystalline Xylene (Dimethylbenzene). By PAUL JANNASCH.*

HÜBNER and Wallach's discovery of a crystalline monobromotoluene rendered a revision of the syntheses of various aromatic hydrocarbons effected by Fittig's method desirable. The investigation of a trimethylbenzene prepared from a chemically pure compound as point of departure, appeared, by reason of the marked and singular property possessed by the trimethylbenzene hitherto investigated of yielding on oxidation with dilute nitric acid two well characterized monobasic acids, of especial value towards elucidating and establishing the views on the origin of these compounds.

For this purpose, then, a chemically pure dimethylbenzene was requisite; this the author obtained by acting on perfectly pure crystalline bromotoluene with methyl iodide and sodium. On distilling the product, the remarkable observation was made that crystals separated from the distillate between 135°—137°, and it was then found that simple cooling with water sufficed to cause an almost total solidification of the hydrocarbon. The crystalline mass was then further cooled in a freezing mixture, the small quantity of liquid poured off, the cake broken up and well pressed between bibulous paper. The crystals, after drying for several hours over sulphuric acid, boiled constantly at 136° and melted immediately at 15°; analysis proved their composition to be C_8H_{10}. Further communications on this solid dimethylbenzene and its derivatives are promised.

H. E. A.

On Tetranitro-Diphenyl. By S. M. LOSANITSCH.†

THIS body is formed by dissolving dinitrodiphenyl in fuming nitric acid or by acting on diphenyl with a large excess of a mixture of equal volumes of concentrated sulphuric and nitric acids. On adding water to these solutions, it separates as an amorphous mass, which is sparingly soluble in alcohol, more readily in ether, from which solvents however, it does not crystallise; it could only be obtained as a friable amorphous mass, which melts at 140°.

By treating it with ammonium sulphide or with tin and hydrochloric acid, a mixture of amido-compounds is obtained which could

* Zeitschr. f. Chem. [2], vii, 117. † Deut. Chem. Ges. Ber., iv, 404—406.

not be separated, as they are still more difficult to purify than the nitro-compound itself.

C. S.

On Ditolyl. By TH. ZINCKE.*

THE *benzyltoluene* $C_{14}H_{14}$, described by the author in his previous communication (p. 508), bears a strong resemblance to ditolyl, which Fittig obtained by acting with sodium on *crude* bromtoluene. Now as this body is a mixture of two isomerides, and as Fittig had diluted it with benzene hydrocarbons, the hydrocarbon obtained from it might either be a ditolyl of which six isomeric modifications are possible; or the benzene hydrocarbons took part in the reaction, just as in that by which benzyltoluene is formed and then it is either identical with this hydrocarbon or a second modification. To clear up these points the author has commenced the study of the ditolyls.

Sodium acts very briskly on a solution of solid bromotoluene in anhydrous ether, and if it is not well cooled, hydrogen is evolved and a large quantity of toluene is regenerated, the formation of which however, cannot be completely evaded, even if the vessel is surrounded by a freezing mixture. The other products of the reaction are a large quantity of a yellow solid (not further studied), which is sparingly soluble in alcohol, and can thus be easily separated from two isomeric ditolyls which dissolve readily in alcohol. That which is present in the largest quantity is a solid, which crystallises from ether in splendid monoclinic prisms and from alcohol in white plates melting at 121°. The second ditolyl is a liquid, having an aromatic smell and boiling at 283°—288°, whilst that obtained by Fittig boils at 272°.

By acting with sodium on crude bromo- and chloro-toluene, only a small quantity of the solid ditolyl is obtained; the chief product is a liquid, which appears to be identical with Fittig's ditolyl; that prepared from chlortoluene boiled at 273°—278°.

The author has begun to study the oxidation-products of these different hydrocarbons and thus hopes to get an insight into their chemical structure.

C. S.

On certain Tolane Compounds. By LIMPRICHT AND SCHWANERT.†

BY the action of phosphoric chloride (containing oxychloride) on toluylene, two isomeric bodies of formula $C_{14}H_{10}Cl_2$ are produced, iden-

* Deut. Chem. Ges. Ber., iv, 396—400. † Deut. Chem. Ges. Ber., iv, 379.

tical with the two recently obtained by Zinin by the action of zinc on tetrachlorobenzil, $C_{14}H_{10}Cl_4$, their melting points being respectively 63° and 153°, and treatment with sodium amalgam forming tolane in each case; alcoholic potash also forms tolane and potassium chloride; distillation, or heating with glacial acetic acid and silver acetate, converts a portion of each modification into the other one, no acetyl compound being formed in the latter case: they do not unite with bromine.

Tolane similarly treated with phosphoric chloride forms in like manner two modifications of formula $C_{14}H_9Cl_3$, melting at 137°—145° and 150° respectively.

With bromine, tolane similarly forms two isomeric compounds $C_{14}H_{10}Br_2$, melting at 64° and 200°—205° respectively (the former having been previously obtained by Jena). By long continued heating with water at 170°—180°, each modification is to a great extent converted into the other, whilst by dry distillation the one of higher melting point is for the most part transformed into the other, but the one of lower melting point is not thus changed into that of higher melting point. At 200° the action of water is

$$2C_{14}H_{10}Br_2 + 2H_2O = C_{14}H_{10} + C_{14}H_{10}O_2 + 4HBr,$$

benzil and tolane being thus produced.

Treatment with silver acetate forms a mono-acetate, $C_{14}H_{10}Br(C_2H_3O_2)$ but from this no alcohol was obtainable, a temperature of 140°—150° (in presence of water) splitting up the compound into acetic and hydrobromic acids, tolane, and benzil: fusion of sulphotolanic acid with caustic potash failed to produce the alcohol.

C. R. A. W.

On the Carbonic and Alcoholic Fermentation of Sodium Acetate and Ammonium Oxalate. By A. Béchamp.*

This is an attempt to produce alcohol from "almost mineral" compounds, incapable of producing sugar, and free from any matter already fermenting.

I. A. 300 grams of pure neutral sodium acetate and 2500 c.c. of water were left in a phial closed with paper from February, 1864, to May, 1868. The fungoïd growths in the liquid weighed 0·15 grm., consisting of microzymes, bacteria, and a thin mycelium of entangled filaments. From the very alkaline filtrate, repeated distillation over dry potassium carbonate isolated 0·6 c.c. of alcohol, recognized by its flame and by its oxidation with chromic acid. The residue, after sodium acetate had crystallised out, required for neutralization 115 c.c. of standard sulphuric acid (containing 4·86 per cent. of H_2SO_4), showing

* J. Pharm. [4], xiii, 5—9.

that 6·85 grams of acetic acid had disappeared. Much carbon dioxide escaped. The distillate gave a sodium salt containing a trace of formic acid.

B. In May, 1868, to ascertain the part played by air, sodium acetate 100 grm., pure calcium carbonate and phosphate, of each 0·1 grm., ammonia alum 0.07 grm., water 2,000 c.c., were left for a week in a phial closed with paper, and then a delivery tube dipping into water was attached. When the water had risen to a constant level, the gas in the phial was collected, and proved to be nitrogen. The capacity of the whole being 450 c.c., 94·5 c.c. of oxygen had been absorbed. On distilling, alcohol was obtained, while the residue required 14·4 c.c. of sulphuric acid (of 4·86 per cent); consequently 0·86 grm. of acetic acid had disappeared. Carbon dioxide was again evolved. To oxidize 0·86 gram of acetic acid, ·917 grm. or 641 c.c. of oxygen are required. But the air gave only 95 c.c. To form alcohol also requires hydrogen: hence water must be decomposed. The author is investigating this point.

II. In October, 1868, pure neutral ammonium oxalate 65 grm., water 2,000 c.c., were placed in a phial; in April, 1869, the mixture had become mouldy and very alkaline. The dried moulds weighed 0·08 grm., consisting of mycelium, oval cells, and microzymes: no bacteria. The filtrate took for neutralisation 2·03 grm. of oxalic acid, and gave off carbon dioxide. Hence 2 grm. of oxalic acid had been destroyed. By distillation 0·3 c.c. of alcohol was obtained.

In another case all the oxygen of the air was absorbed, but did not account for the destruction of oxalic acid. In both cases a little acetic acid was formed.

These two salts, therefore, give alcohol and carbon dioxide, besides in the one case formic, and in the other acetic, acid. Water is probably decomposed. But as the oxalate does not contain any group of atoms having the structure of alcohol, the moulds must have synthesized the matter of their tissues, and then excreted alcohol and other products.

III. Pure distilled water, kept for six months in a stove in a phial closed with paper, developed microzymas, bacteria, and mycelium. Alcohol, volatile acid, and ammonia were obtained. When moulds were absent, none of these products appeared. Here water, carbon dioxide, and air cannot have fermented; but the moulds in growing have, by synthesis of their own substance, produced the alcohol which they have afterwards excreted. E. T. C.

On the Chlorine Derivatives of Ethyl Chloride. By A. Geuther.*

The action of chlorine on ethyl chloride and on mono- and di-chlorethyl chlorides, does not yield derivatives of the composition $C_2H_2Cl_4$ and

* Zeitschr. f. Chem. [2], vii, 147; from Jenaische Zeitschr, vi, 238.

C_2HCl_5, boiling respectively at 102° and 146°, their place being taken by the analogous derivatives of ethene chloride boiling at 135° and 153°·5. It is notable that a product boiling at 115°, identical with mono-chlorethene chloride is also produced; this substance was traced back to ethene chloride which was found in small quantities. The author attributes the formation of the latter to alcohol vapour in the ethyl chloride he employed. Mono-chlorethyl chloride and aldehyde chloride have the same boiling point.

F. H. H.

On the Chloro-substitution Products of Ethyl Oxide. By OSCAR JACOBSEN.*

THE first product of the action of chlorine on ether is a true monochlorethyl oxide. This is identical with the body which Wurtz and Frapolli† obtained by the action of hydrochloric acid on an alcoholic aldehyde solution, and commonly termed *aldehyde-ethyl-chloride*. Pure monochlorethyl oxide boils at 97°—98°. With sodium ethylate it yields acetal; sulphuric acid decomposes it with formation of sulphovinic acid, hydrochloric acid, and aldehyde. Its formula is therefore $\left\{\begin{array}{l} CHCl.CH_3. \\ O \\ CH_2CH_3. \end{array}\right.$ By the action of water it yields a liquid boiling slightly below 50°, of the composition $\left\{\begin{array}{l} CH.OH.CH_3 \\ O \\ CH_2.CH_3 \end{array}\right.$; this, corresponding to the analogous compound of chloral, may be termed *aldehyde-alcoholate*. Condensation-products are formed at the same time, the first of which, boiling between 80° and 84°, appears to be $\left\{\begin{array}{l} CH.OC_2H_3.CH_3. \\ O \\ CH.OC_2H_3.CH_3. \end{array}\right.$

Lieben‡ has shown that in dichlorethyl oxide, both chlorine-atoms are in one ethyl-group, but has left it undecided which of the three formulæ—

$$\left\{\begin{array}{l} CH_2.CHCl_2 \\ O \\ CH_2.CH_3 \end{array}\right. \qquad \left\{\begin{array}{l} CHCl.CH_2Cl \\ O \\ CH_2.CH_3 \end{array}\right. \qquad \left\{\begin{array}{l} CCl_2.CH_3 \\ O \\ CH_2.CH_3 \end{array}\right.$$

belongs to it. By treatment with sulphuric acid, dichlorethyl oxide is easily and perfectly decomposed, sulphovinic acid, hydrochloric acid, and monochlor aldehyde being formed. Sodium ethylate converts in into monochloracetal, which later compound is identical with Lieben's

* Ber. Deut. Chem. Ges. iv, 216—218. † Ann. Chem. Pharm., cviii, 226.
‡ Ann. Chem. Pharm., cxlvi, 232.

ethoxylchlorethyl oxide, as was indeed already surmised by him.* This proves $\left\{\begin{array}{l}CHCl.CH_2Cl\\O\\CH_2.CH_3\end{array}\right.$ to be the true formula for dichlorethyl oxide,† and $\left\{\begin{array}{l}CH_2Cl\\CH.OC_2H_3.OC_2H_5\end{array}\right.$ to be that for monochloracetyl. By the action of water on dichlorethyl oxide, monochloraldehyde alcoholate $\left\{\begin{array}{l}CH_2.Cl.\\CH.OH.OC_2H_5,\end{array}\right.$ boiling at 95—96° is formed. Of the condensation-products simultaneously formed, especially on warming, the first can be distilled unchanged at about 165°, and has the composition $\left\{\begin{array}{l}CH.OC_2H_5.CH_2Cl.\\O\\CH.OC_2H_3.CH_2Cl.\end{array}\right.$. This body corresponds to Glinsky's monochloraldehyde hydrate,‡ $C_2H_3ClO + \frac{1}{2}H_2O$, the constitution of which is, no doubt, represented by the formula $\left\{\begin{array}{l}CHOH.CH_2Cl\\O\\CHOH.CH_2Cl.\end{array}\right.$

A *trichorethyl* oxide cannot be separated in a state of purity by fractional distillation, as the dichlorethyl oxide is the highest chloro-product which can be distilled unchanged. Its presence in the product of the action of chlorine on ether can, however, be proved indirectly. If indeed by the action of sodium ethylate on the residue remaining above 155° on the distillation of the crude dichlorethyl oxide, a mixture of chlorinated acetals be prepared, it will be possible to isolate moderately pure dichloracetal from this by fractioning. A product boiling at 180°—187° contained 37·2 per cent. chlorine—dichlorethyl oxide contains 380 per cent.—and on decomposition with sulphuric acid gave dichloraldehyde. This proves the constitution of trichlorethyl oxide to be represented by $\left\{\begin{array}{l}CHCl.CHCl_2.\\O\\CH_2.CH_3.\end{array}\right.$

Malaguti described the liquid which he obtained by the action of chlorine on ether at 90°, as *tetrachlorethyl oxide.* A tetrachlorethyl oxide of the formula $\left\{\begin{array}{l}CHCl.CCl_3\\O\\CH_2.CH_3\end{array}\right.$ should yield chloral on treatment with sulphuric acid, and, in fact, Malaguti observed the formation of this body, but he wrongly considered it to be a bye-product present in in his crude tetrachlorethyl. When the action of chlorine on ether at

* Deut. Chem. Ges. Ber. iii, 911.

† The same formula has been proposed by Abeljanz (Deut. Chem. Ges. Ber. iv, 61). Lieben's statement that phosphorus pentachloride is without action on dichlorether in the cold or at a gentle heat, the author finds is perfectly correct.

‡ Ber. Deut. Chem. Ges. iii, 870.

90° is purposely not pushed too far, a liquid is obtained which yields a considerable quantity of chloral on treatment with sulphuric acid, and consequently contains a tetrachlorethyl of the above constitution.

The true end-product of the action is not tetra- but *penta-chlorethyl* oxide. This is a colourless, somewhat thick liquid, of sp. gr. 1·645. Its reactions show that here also one ethyl-group has remained intact, and that its constitution is therefore expressed by the formula $\left\{\begin{array}{l} CCl_2.CCl_3 \\ O \\ CH_2.CH_3 \end{array}\right.$. The substitution is first extended to both ethyl groups under the influence of sunlight. The numbers in the formula

$$\underbrace{CH_3.CH_2,O.CH_2.CH_3}_{2.3.4\ 1\ 5}$$

express the order in which, according to the preceding, the hydrogen atoms in the first ethyl group are successively replaced.

H. E. A.

On Tribasic Acetic Ether. By A. Geuther.*

Sodium ethylate, free from alcohol, was heated in the tube in which it had been prepared (*Zeitschr.* iv., 652) with an equivalent quantity of dichlorinated ethyl chloride—boiling point, 72°—75°—and a quantity of anhydrous ether at least equal in volume to that of the sodium ethylate employed, for twelve hours at 100°—120°, until the whole of the sodium ethylate had been converted into granular sodium chloride. On opening the tube before the blow-pipe, a gas burning with a green flame escaped; after treating the contents of the tube with water, and separating the ethereal and aqueous layers, washing the former once with twice its volume of water, drying over calcium chloride, and distilling off the ether, the undecomposed chlorinated body, and the acetic ether formed in the reaction, a liquid residue remained consisting chiefly of two products, the one containing chlorine and boiling at about 142°, the other free from chlorine and boiling at about 122°.

1. *Monochlor-ethoxyl-ethylene*, $C_2H_2Cl(OC_2H_5)$.—This body, after purification by repeated distillation, forms a colourless, inflammable liquid, insoluble in water, of peculiar pleasant smell. It boils at 122°—123°, and has a sp. gr. of 1·02 at 22°.

2. *Tribasic acetic ether*, $CH_3C(OC_2H_5)_3$.—This body, which was analysed, although not obtained in a perfectly pure state, is a colourless, inflammable liquid, of peculiar but pleasant ethereal odour, different from that of acetic ether. Sp. gr. = 94 at 22°. On heating with water in a sealed tube to 120°—130°, it was decomposed into alcohol and acetic ether.

* Zeitschr. f. Chem. [2], vii, 128; from Jenaische. Zitschr. 1871, 221.

Besides these products, acetic ether and sodium acetate are formed in the reaction. The former is present in the portion of the ethereal layer distilled over on the water-bath, and may be separated by rectification; the latter is found in the wash-water.

H. E. A.

Normal Butylic Alcohol. By LIEBEN and ROSSI.*

THE first eight pages of this memoir are occupied by an account of the discovery and investigation of the properties of the alcohols of the ethylic series by Wurtz, Friedel, Ritter, Limpricht, Erlenmeyer, Wanklyn, and others. The authors quote the observation of Williamson that the aldehydes may be prepared by distilling a salt of the corresponding acid with a formate. Some doubt was thrown on the universality of this method by the failure of Siersch to obtain propionic aldehyde thereby. The authors offer an explanation of this observation of Siersch, but deny that the aldehyde cannot be so obtained.

Preparation of Butyric Aldehyde.—It was first necessary to obtain pure butyrate of calcium; the authors therefore prepared butyric acid by fermentation, but found the acid so obtained, as well as some purchased as pure butyric acid, to be impure. By fractional distillation it may be approximately but not perfectly freed from the acids of higher and lower boiling point. To purify the acid, the authors recommend that the fraction boiling between 155° and 165°, or by still more careful work that boiling between 159° and 164°, be dissolved in water, and the insoluble oil consisting of the higher acids, in case such should be present, separated off, and then by the addition of milk of lime the acid converted into a lime salt. On evaporation the lime salt separates as a crust on the surface, and may be skimmed off. This lime salt is less soluble in hot water than in cold, and is not very readily moistened. This concentration and removal of the salt is carried on for a longer or shorter period according to the purity of the butyric acid used; the last mother-liquors do not, as a rule, yield more of a pure product.

The boiling-point of butyric acid thus purified was found to be 163·2° at a pressure of 748·7 mm. of mercury.

The authors employed this nearly pure butyrate of calcium after it had been well pressed and air-dried; they mixed it intimately with its own weight of calcium formate, dried the mixture at about 100°, and then distilled it in small portions of about 10 grams out of small glass retorts, both the sides and bottoms of which were heated with charcoal. Both gases and vapours were evolved during the distilla-

* Ann. Ch. Pharm., clviii, 137—180.

tion; the mass melted imperfectly, and after about twenty minutes heating, left a fritted mass of calcium carbonate in the retort. The authors state that they have employed altogether some kilograms of calcium butyrate in this and the following researches.

The product condensed from these distillations is a brownish liquid, possessing a suffocating aldehyde-like, but at the same time somewhat empyreumatic odour; generally, a small layer of water is present, as it is not easy to dry large masses of the calcium-salts perfectly; the product is about half the weight of the calcium butyrate employed. On fractionally distilling it, the boiling-point rose from 50° to 200°; and by repeated distillations, a fraction boiling between 70° and 80° was obtained, which was nearly pure butyric aldehyde. This fraction was about half the crude product. The other half consisted partly of aldehydes, particularly those of lower boiling-point, but chiefly of substances boiling above 130°, which are not aldehydes, and which, provisionally, were not more closely examined. The authors convinced themselves that the amount of aldehydes, other than butyric aldehyde, was extremely small when pure butyrate of calcium was employed; they cannot confirm the statement of Michaelson that propionic aldehyde is formed together with butylic aldehyde by the dry distillation of the butyrate and formate of calcium; they also imagine that the very complicated result obtained by the distillation of calcium butyrate alone is in great measure due to the use of impure butyric acid. Normal butyric aldehyde possesses the characteristic penetrating, slightly cough-provoking aldehyde smell; it reduces silver oxide and dissolves in about 27 parts of water; boils at about 75° C. The authors did not take much trouble to obtain it pure, as it was required for the preparation of the alcohol, and the purification could be more readily effected at a later stage of the operations, more particularly by the fractional distillation of bromide and iodide of butyl.

The authors did not find bisulphites available for the purification of the butyric aldehyde; they were of course useless for the separation of the lower aldehydes, and the bodies of higher boiling-point could be readily separated by fractional distillation; moreover, there was danger of losing the product. The authors cannot at present say with certainty whether the bisulphite or the substances ordinarily used for the liberation of the aldehyde from the crystalline bisulphite-compound are to blame; but at any rate bodies of higher boiling-point are formed. They consider it very probable that Siersch's negative result was entirely due to the treatment of the crude aldehyde with bisulphite.

Butylic Alcohol.—To convert the butyric aldehyde into alcohol, the former, in aqueous solution, was treated with sodium amalgam, care being taken that the liquid never had an alkaline reaction. The operation succeeds best with small quantities. Ten grams of the

aldehyde are treated with 250 grams of water, that is nearly, but not quite enough to effect its solution. This mixture was treated successively with seven portions of 100 grams of 1 per cent. sodium amalgam. Theory requires 6·4 grams of sodium. The equivalent quantity of sulphuric acid was added at the same time as the sodium amalgam. The reaction of the liquid was always somewhat acid. When the action was ended, the liquid was distilled and the distillate again treated with 300—400 grams of sodium amalgam, together with the same quantity of sulphuric acid as above. The liquid is again distilled and the products of the several operations purified together.

A small quantity of insoluble oil, which always forms during the operation, is removed by filtration through wet filter-paper, and the butylic alcohol is separated from the filtrate by a series of distillations. The butylic alcohol passes over with the first portions of the water. 100 grams of butylic aldehyde gave in different operations 80—90 grams of crude wet butyric alcohol. This product was dried as perfectly as possible with fused carbonate of potash; by far the largest quantity distilled between 110° and 120°, and it was easy to obtain the pure alcohol from the fraction which boiled between 113° and 117°. It is very difficult to remove the last traces of water from the butylic alcohol*. This may, however, be effected by digestion, first with lime or baryta, and then by repeated distillation from sodium.

Three combustions of the butylic alcohol are quoted, the first two of which were of a substance evidently contaminated with a small quantity of water. The numbers were as follows:—

* In a note signed Lieben, the different methods of drying alcohols are discussed. Melted potassium carbonate and anhydrous copper sulphate were not found capable of drying the alcohol. The sulphate remained unaltered in butylic alcohol containing two per cent. of water. Lime and baryta act better; but one treatment even with a considerable quantity of lime is seldom sufficient to effect the object. With respect to sodium it has been frequently pointed out, especially by Chapman, that it does not confine its action to the water in the alcohol, but at the same time acts on the alcohol, and produces an alcoholate, and water will be found in the distillate, even though there be more than sufficient sodium present to combine with all the water. This observation is quite correct; but Chapman's conclusion that, therefore, sodium is not available for drying alcohols is not confirmed, as Lieben finds that the best method of drying alcohols is to distil them repeatedly from small quantities of sodium. He observes that it is necessary to heat the alcohol far above its boiling-point in an oil-bath to separate it from the alcoholate.†

† *Note by the Abstractor.*—At any rate, in the case of amylic alcohol, this method of drying is not available, as the hydrate of sodium, when distilled with large excess of amylic alcohol, is completely decomposed into amylate and water. Common alcohol may be dried as above, but propylic and butylic alcohols from fermentation, certainly not without great difficulty. On the other hand caustic baryta dries these compounds perfectly.

	I.	II.	III.	Calculated.
Carbon	64·35	64·3	64·71	64.86
Hydrogen	13·41	13.53	13·33	13·51
Oxygen	—	—	—	21·63
Vapour-density of the substance by experiment				2·65
By theory				2·56

Normal butylic alcohol is a colourless liquid, the smell of which resembles that of the butylic alcohol of fermentation, but is somewhat weaker and more spirituous. It is not miscible with water, and, like the aldehyde, requires a large excess of water to dissolve it. It is soluble in aqueous hydrochloric and hydrobromic acids.

The boiling-point is 116° at a pressure of 740 mm. The specific gravity, as compared with that of water of the same temperature, is as follows:—

At.....	0°	20°	40°	99·1
Sp. gr.....	0·8242	0·8108	0·7998	0·7734

Another specimen of the alcohol obtained from the pure iodide by converting first into acetate and then into alcohol, gave

At	0°	20°	40°	98·9°
Sp. gr.....	0·8239	0·8105	0·7994	0·7735

This specimen of alcohol gave on combustion, carbon 64·72, instead of 64·86 as required by theory.

Sodium dissolves in the alcohol, evolving hydrogen and forming a glistening mass of needles of the alcoholate. This compound dried in the oil-bath yields a body which appears to consist of sodium butylate, $NaOC_4H_9$.

Oxidation of the Alcohol.—This was performed in the manner previously adopted by one of the authors in the oxidation of the secondary butylic alcohol.*

The products of the oxidation were butyric aldehyde and *normal* butyric acid, exclusively.

Some products obtained in the purification of the aldehyde, probably by the action of the reagents employed upon it, also yielded butyric acid on oxidation. The fractions of lower boiling-point obtained by the distillation of the mixed butyrate and formate of calcium contained, as remarked above, traces of lower aldehydes; these were converted by the action of nascent hydrogen into the corresponding alcohols, and finally into the iodides. The presence of ethyl iodide was rendered very probable; that of methyl iodide was proved. The latter probably owed its origin to the formation of formic aldehyde by the destructive distillation of the formate employed.

Butyl Chloride.—Prepared by saturating the crude butylic alcohol, surrounded by a freezing mixture, with hydrochloric acid gas; the alcohol

* Ann. Ch. Pharm., cl, 115—118.

absorbs about two-thirds of its weight of the gas, and, if it be pure and dry, the product is not coloured during the operation; in the contrary case, it becomes brown. The saturated alcohol was sealed up in glass tubes with a small quantity of fuming aqueous hydrochloric acid, and heated first to 70°, finally to 100°, until the homogeneous liquid divided itself into two layers, the relative volumes of which did not alter. The lower layer consisted of aqueous hydrochloric acid, the upper one of butyl chloride. The latter washed with strong hydrochloric acid, then with an alkali, and finally with pure water, dried with chloride of calcium, and fractionally distilled, readily yielded a pure product. The chloride is a colourless liquid, insoluble in water, boiling at 77·6° at a pressure of 741·3 mm. Its specific gravity is, as compared with water at the same temperature, 0·9074 at 0°, and 0·8874 at 20°.

Butyl Bromide.—Prepared in a manner exactly similar to that employed for the production of the chloride.

Boils at 100·4° C., at a pressure of 744· mm.

	0°	20°	40°
Specific gravity	1·305	1·2792	1·2571

Butyl Iodide.—Prepared either by the action of hydriodic acid on the alcohol, or by treating the latter with iodine and amorphous phosphorus, as in the well-known method of preparing iodide of ethyl. If prepared from an impure alcohol, it can be readily purified by fractional distillation.

Boils at 129·6° C., at a pressure of 738·2 mm.

	0°	20°	40°
Specific gravity	1·643	1·6136	1·5894

Butyl-ethyl Ether and Butylene.—The behaviour of normal bromide and iodide of butyl to silver salts, and particularly to alcoholic potash, has a general interest, inasmuch as it is connected with the question as to whether the decomposition of the alcoholic iodides into the olefine and hydriodic acid may be used as a characteristic of given classes of alcohols or not. The iodide and bromide both liberate some butylene when they act on alcoholic potash; the quantity is however comparatively small. In the same way, silver salts, by their action on normal butyl iodide, yield traces of butylene. It appears, therefore, that we cannot regard the non-splitting up of the iodide into butylene and hydriodic acid by the action of alcoholic potash, as characteristic of the normal alcohols; nevertheless the normal alcohol yields much less butylene than the others.

The authors heated bromide of butyl with $1\frac{1}{2}$ times the theoretically requisite quantity of sodium alcoholate, which was wetted with absolute alcohol, in a sealed tube to 110°. On opening the tube in the cold, no gas was evolved, but on warming, a small quantity of butylene

escaped; the chief product was butyl-ethyl-ether. A somewhat larger quantity of butylene is obtained when an excess of alcoholic potash acts on the bromide or iodide of butyl.

Ten grams of normal butyl iodide were treated in a flask with a solution of 5 grams of potash in 15 grams of alcohol of 90 per cent., and 5 grams of powdered solid potash were added. The flask was connected with an inverted condenser, a tube from the upper end of which passed into a condensing apparatus cooled by a freezing mixture. A reaction first commenced on warming, and was rather vigorous, rather more than 1 c.c. of liquid butylene being collected; and by appropriate treatment of the residue in the flask $3\frac{1}{2}$ grams of butyl-ethyl ether were obtained, so that, notwithstanding the large excess of potash, only one-third of the butyl iodide was decomposed into butylene.

The authors state that ethyl iodide treated in the same way as the above mentioned butyl iodide, yields a small quantity of ethylene recognised by converting it into ethylene bromide. Ethyl iodide is therefore decomposed to a much less extent into the olefine than the iodide of butyl; but this experiment shows that the production of the olefine from the iodide does not constitute an absolute but only a relative difference between the iodides. The butylene evolved from iodide of butyl easily unites with hydriodic acid, forming a compound which boils between 115° and 120°, and readily yields butylene by its action on silver acetate. The compound so produced is, in fact, iodide of secondary butyl.

Butyl-ethyl ether is the principal product of the action of iodide or bromide of butyl on alcoholic potash or sodium ethylate. The ether boils at 91·7° under pressure of 742·7 mm.

	0°	20°	40°
Specific gravity	·7694	·7522	·7367.

Butyl acetate is obtained by the action of butyl iodide on silver acetate in the presence of glacial acetic acid. The action takes place readily, traces of butylene being formed at the same time. Butyl bromide may be used instead of the iodide; the reaction is somewhat slower, but in both cases complete, the product containing no trace of bromine or iodine. The authors publish this fact, as Chapman and Smith state that it is extremely difficult to obtain the complete decomposition of normal bromide of propyl, either with acetate of potassium or with acetate of silver.*

Butyl acetate is a sweet fruity-smelling liquid, boiling at 125·1°, under a pressure of 740 mm.;—

* Chem. Soc. J. [2], vii, 193.

	0°	20°	40°
Specific gravity	0·900	0·8817	0·8659

Butyl butyrate, prepared in a similar way to the acetate, is a colourless liquid of agreeable odour, boiling at 165·5° at a pressure of 735·7:—

	0°	20°	40°
Specific gravity	0·8885	0·8717	0·8579.

Butyl cyanide is obtained by the action of either bromide, chloride, or iodide of butyl on cyanide of potassium, the materials being digested with alcohol in a sealed tube at 110° for two days.

Boiling-point, 140·4°, at pressure of 739·3 mm. Sp. gr. at 0°, 0·8164.

The chief interest which the authors had in this body was to obtain valerianic acid from it. They, therefore, did not examine it very closely, and the specimen they obtained appears to have been slightly impure.

Butylamine.—Butyl chloride was digested with solid potassium cyanate and alcohol, in sealed tubes, for two days, at a temperature of 100°—110°. The alcoholic liquid was then digested for two days with caustic potash; the liquid distilled to dryness; water added to the residue, which was again distilled; the two distillates mixed, acidulated with hydrochloric acid, and evaporated to dryness; the dry residue exhausted with alcohol, which dissolved the chlorides of the organic bases and left ammonium chloride; and the alcoholic extract was evaporated to dryness and distilled with lime from a combustion-tube, the front part of which contained anhydrous barium oxide. The base was also obtained as a by-product in the preparation of normal valerianic acid from the cyanide; both products contained both di- and tri-butylamine. The butylamine could be separated by fractional distillation, but the di- and tri-butylamines not so readily.

Butylamine is a colourless, very hygroscopic, ammoniacal-smelling, fuming liquid, the vapour of which produces a feeling of heat on the skin. Both cork and caoutchouc are strongly attacked by the vapour. It is miscible in all proportions with water, and the solution precipitates lead, aluminium, magnesium, copper, and silver salts. The copper and silver precipitates are soluble in excess of the base, and the aluminium precipitate appears to be so likewise. The boiling-point is 75·5° at pressure 740 mm.; it is not quite constant.

	0°	20°
Specific gravity at	0·7553	·7333

The platinochloride of butylamine crystallises in golden-yellow plates, slightly soluble in cold, moderately soluble in hot water; soluble also in alcohol.

Dibutylamine, boiling at about 160°, forms with platinic chloride a compound crystallising in long yellow needles, which melt in warm water, are soluble in hot, but very slightly soluble in cold water.

Tributylamine forms with platinic chloride, a compound crystallising in groups of small needles which melt and are slightly soluble in warm, very slightly in cold water, but soluble in alcohol.

The four known butylic alcohols are distinguished by their boiling-points, thus:—

Primary Butylic Alcohols.

Normal butylic alcohol.

$$C\begin{cases}CH_2CH_2CH_3\\H\\H\\OH\end{cases}$$

boils at 116°.

Butylic alcohol of fermentation.

$$C\begin{cases}CH(CH_3)_2\\H\\H\\OH\end{cases}$$

boils at 109°.

Secondary butylic alcohol.

$$C\begin{cases}CH_2,CH_3\\CH_3\\H\\OH\end{cases}$$

boils at 99°.

Tertiary butylic alcohol.

$$C\begin{cases}CH_3\\CH_3\\CH_3\\OH\end{cases}$$

boils at 82°.

The derivatives also show similar differences of boiling-point.

The authors conclude that normal alcohols are distinguished from their isomerides by the following characteristics:—1. They possess the highest boiling-points and the greatest stability. 2. Their ethers, both simple and compound, also the ammonia base, possess the highest relative boiling-points, and the haloïd compounds show the least tendency to evolve the olefine. 3. By oxidation the alcohol yields an acid of the same number of carbon-atoms as itself contains. This acid is distinguished from other isomeric acids by its higher boiling-point, and apparently also by its greater power of resisting oxidation.

E. T. C.

On Propyl and Butyl Bromides. By Is. Pierre and Ed. Puchot.*

Propyl Bromide, C_3H_7Br.—To 100 pts. pure propyl alcohol are added alternately in small quantities 15 pts. phosphorus and 145 bromine, in a balloon with a long neck, keeping the phosphorus in excess, and the whole in constant agitation. The liquid decolorizes, and evolves hydrobromic vapours towards the last. It is then distilled, collecting all below 110°. From the residue in the retort, water separates

* J. Pharm. [4], xiii, 9.

a little more crude bromide. The distillates are shaken repeatedly with water and crushed marble, to remove acid, then decanted, dried by calcium chloride, and fractionated, rejecting the first and last drops of each distillation.

This ether is mobile, colourless, and has the pleasant but slightly alliaceous odour peculiar to the chlorine group, even when phosphorus is not used. It boils at 72°. In contact with air, especially if moist, it becomes coloured. Sp. gr. at 0°, 1·3497; at 30·15°, 1·301; at 54·2°, 1·2589. From this we may calculate the sp. gr. at any temperature between 0° and 72°, and the relative volumes, taking as unity the vol. either at 0° or at 72°. [Here follows a table calculated from these data, of the specific gravities and volumes for every 10°.] As in most liquids, the co-efficient of expansion increases as the temperature rises.

Butyl Bromide, C_4H_9Br. To 120 pts. pure butyl alcohol are added the same quantity of phosphorus and bromine, with the same precautions as above. What distils below 120° is collected and purified as above described. In properties it closely resembles propyl bromide. It boils at 90·5°. Sp. gr. at 0°, 1·249; at 40·2°, 1·191; at 73·5°, 1·1408. [Here follows a calculated table similar to the one with *propyl bromide*.*] This confirms the statement made by the authors twenty years ago, that between the same limits the expansibility of a liquid is greater the lower the boiling point. [Here follows a table, calculated from the above data, of the contraction of alcoholic bromides, for every 10° starting from their boiling-points, showing that the most volatile contract most rapidly.]

E. T. C.

Behaviour of Normal Butyl Iodide with Alcoholic Potash.

By A. and M. Saytzeff.‡

The authors have found that the products of the action of potash in alcoholic solution on normal butyl iodide are butylene and butyl-ethyl ether. Their mode of proceeding was as follows:—100 grams of butyl iodide were added gradually to a boiling mixture of 200 grams of potassium hydrate and 150 grams of 90 per cent. alcohol. This mixture was contained in a flask connected with the lower end of a

* Wurtz gives 89° as the boiling point of butyl bromide, and 1·274 as the sp. gr. at 16°, while the authors have found it to be 1·226. They attribute this to a trace of lower ethers in Wurtz's bromide.†

† *Note by the Abstractor.*—Messrs. Chapman and Smith found the sp. gr. of butyl bromide to be 1·270 at 16° (a very large quantity of a lower bromide would be required to raise the sp. gr. from that found by the authors to that found by Wurtz). The sp. gr. of propyl bromide does not agree with that obtained by Fittig, or by Chapman and Smith.

‡ J. pr. Chem. [2], iii, 88.

condenser. The butylene evolved in the reaction was conducted from the upper end of the condenser through a wash-bottle of water into a gas-holder; the volume obtained from the above quantity of iodide was in one experiment 2·8, and in another 3·5 litres.

The alcoholic liquid in the flask separated, on addition of water, into two layers, the upper of which, having a distinct ethereal odour, was separated, washed with water to free it from alcohol, dried over calcium chloride, and treated with sodium. This liquid distilled almost entirely between 85° and 95°. The portion boiling between 91° and 94°, after being again treated with sodium, distilled, for the most part, at 91·5°—92·5°, and gave on analysis 70·04 per cent. C. and 14·10 H., the formula $C_6H_{14}O$ requiring 70·58 per cent. C. and 13·72 H.

The body thus obtained was shown to be butyl-ethyl ether by decomposing it with hydriodic acid at 100° in a sealed tube. It thus yielded a heavy oil, which was resolved by fractional distillation into two portions, boiling at about 72° and 130°, the boiling-points of ethyl iodide and butyl iodide respectively.

Butyl-ethyl ether is a mobile liquid, having an agreeable odour resembling that of ordinary ether. It is nearly insoluble in water. Its sp. gr. at 0° is 0·761, and its boiling-point 91·5°—92·5°.

Butylene obtained from normal butyl iodide, as above described, is at ordinary temperature and pressure a gas, but may be condensed to a mobile liquid by means of a mixture of ice and salt. It possesses the characteristic disagreeable odour of the hydrocarbons of the series C_nH_{2n}. It is rapidly absorbed by bromine.

Normal butyl iodide having the constitution expressed by the formula $CH_3—CH_2—CH_2—CH_2I$, the following four butylenes may be formed by the abstraction from it of the elements of hydriodic acid:

1.	2.	3.	4.
CH_3	CH_3	CH_2'	CH_3
CH_2	CH'	CH_2	CH_2
CH''	CH_2	CH_2	CH_2
CH_2'	CH_2'	CH_2'	CH''.

To determine which of these is the true formula of the butylene obtained by them, the authors investigated the behaviour of the body with hydriodic acid and with hypochlorous acid.

Action of Hydriodic Acid on Butylene.—Butylene combines with hydriodic acid slowly at the ordinary temperature in closed vessels, forming an oily liquid, which distils at 116°—120°. Judging by the boiling-point, this body is either the iodide of methyl-ethyl carbinol (which boils, according to Lieben, at 119°—120°), or the iodide of primary isobutyl alcohol (the boiling-point of which, according to

Wurtz, is 120°, according to Pierre and Puchot 122·5°): in any case it is not normal butyl iodide, that substance boiling at about 130°.

The iodide acts energetically on a mixture of silver acetate and glacial acetic acid, a considerable quantity of butylene being evolved at first. The butyl acetate obtained by distilling the mixture is a pleasant-smelling liquid, boiling at 110°—113°. When heated to 120° with strong potash-ley in sealed tubes it is converted into butyl alcohol, boiling at 97°—100°, and having an agreeable alcoholic odour, quite different, however, from that of primary or tertiary butyl alcohol.

The foregoing facts favour the view that the iodide obtained from butylene and hydriodic acid is secondary butyl iodide. Further evidence in support of this view was obtained by oxidising the alcohol with a mixture of potassium dichromate and sulphuric acid. It thus yielded a body which from its smell (quite unlike that of butyl aldehyde), from the difficulty with which it reduced silver oxide, and from its property of combining with sodium bisulphite, appeared to be a ketone, probably methy-ethyl ketone. It was found, moreover, that only one acid (acetic) was formed in the oxidation, which shows that the body oxidised was a secondary alcohol. Hence there can be little doubt that the iodide is secondary butyl iodide.

Action of Hypochlorous Acid on Butylene.—The authors found that butylene was very slowly absorbed by hypochlorous acid. After the absorption was completed, they destroyed the excess of acid by means of sodium bisulphite and submitted the product to distillation. The aqueous distillate, containing the chlorhydrin of butylene glycol (formed by the direct combination of butylene with hypochlorous acid), was then treated with sodium-amalgam to reduce the chlorhydrin. A small quantity of alcohol was thus obtained, which was oxidised in the same way as the alcohol from the secondary butyl iodide. The acid aqueous distillate, when neutralised with silver oxide, yielded a salt containing 63·48 per cent. of silver (the silver-salt of acetic acid contains 64·67 per cent. of silver), whence it appears that the chief product of the oxidation is acetic acid, and it may be further inferred that butylene likewise yields secondary butyl alcohol by the action upon it of hypochlorous acid. The odour of the alcohol thus obtained was exactly like that of secondary butyl alcohol.

From the above it appears certain that the butylene obtained from normal butyl alcohol yields secondary butyl alcohol by the action of hydriodic acid, and probably also of hypochlorous acid. The former fact alone is sufficient to show that, of the four theoretically possible formulæ for butylene given above, only two, namely, the first and second, are admissible. Which of these is the true constitutional formula remains as yet undecided, but the authors, from certain theoretical considerations, are inclined to prefer the first. That

formula is further supported by the fact first pointed out by Morkownikoff, that, in the elimination of haloid acids from carbon compounds, the hydrogen evolved belongs to the carbon-atom which is in direct combination with that to which the halogen is united. Now normal butyl iodide, having the constitution given above, contains only one carbon-atom in direct combination with that to which the iodine is united, and in accordance with the foregoing rule, must yield, by the elimination of hydriodic acid, a hydrocarbon represented by the formula 1.

J. R.

Additional Observations on Propargylic Ether. By C. LIEBERMANN and O. KRETSCHMER.*

SOME years ago one of the authors† described, under the name of propargylic ether, a compound which was obtained by the action of alcoholic potash on tribrom allyl, and like allylene appears to be the final product of the action of alcoholic potash on various substances. It has been already obtained from $C_3H_5Br_3$ tribromallyl (Liebermann); $C_3H_5Cl_3$ trichlorhydrin (Baeyer); $C_3H_5Cl.Br_2$ monochlorpropylene bromide (Oppenheim); C_3H_5Cl,Br_2 monochlorallyl bromide (Oppenheim); and by the authors from $C_3H_4Cl_2$ dichlorglycide, $C_3H_4Br_2$ allylene dibromide, and by the action of sodium amalgam on propargylic ether dibromide, $C_3H_3Br_2.OC_2H_5$.

The propargylic ether employed in this research was prepared partly from pure crystalline tribromallyl, and partly from trichlorhydrin, by digesting them with an excess of concentrated alcoholic potash. At the completion of the reaction, which took five hours in the case of the tribromallyl and seven with the trichlorhydrin, the alcohol was distilled off, and the first portions which contain the ether collected apart, the receiver being changed as soon as the distillate ceased to give a precipitate with silver nitrate. This last fraction was again rectified in a similar manner. A concentrated solution of silver nitrate was now cautiously added to the alcoholic solution of propargylic ether, and on agitation it became filled with crystalline plates of the silver compound. On adding ammonia to the filtrate, a small quantity more of silver propargylic ether was generally obtained in an amorphous state. The behaviour of dilute alcoholic solutions of propargylic ether towards silver nitrate was probably the cause why Linnemann‡ failed to detect it amongst the products of the action of alcoholic potash on trichlorhydrin. The authors recommend tribromallyl for the preparation of

* Ann. Ch. Pharm., clviii, 230—244. † Liebermann, Ann. Ch. Pharm. cxxxv, 266. ‡ Ann. Ch. Pharm., cxxxix, 19.

propargylic ether in preference to trichlorhydrin, as it is more readily decomposed and also gives considerably more substance.

In order to prepare the pure ether from the silver compound, it was first treated with ammonia to render it amorphous, and then thoroughly washed. On distilling this compound with dilute sulphuric acid, drying with calcium chloride, and rectifying, the ether was obtained pure. The analysis agreed with the formula $C_3H_3.O.C_2H_5$, and a vapour density by Hofmann's method gave 41·8, theory 42·0 (H = 1). The ether is a mobile fluid, lighter than water, and boiling at 80°. It has a penetrating odour, is somewhat soluble in water, and in all proportions in alcohol. Bromine combines directly with propargylic ether without evolution of hydrobromic acid, forming the compound $C_3H_3Br_2O.C_2H_5$, which is heavier than water. This is not acted upon by sodium amalgam in aqueous solution, but in an alcoholic solution the ether is regenerated. It exhibits the same reactions that Morkownikoff* assigns to allylether dibromide, and Tollens† to allyl-alcohol bromide. The authors have found that the ether and its crystalline silver compound obtained from tribromallyl, are identical with those from trichlorhydrin or pure dichlorglycide. They have also studied the action of alcoholic potash on allylene dibromide, the isomeride of dibromglycid. It was prepared by passing allylene evolved from allylene-silver by dilute sulphuric acid, into a solution of bromine in carbon bisulphide, and ascertained to be pure by its boiling-point and by analysis. By long digestion with alcoholic potash, it was decomposed, yielding propargylic ether.

According to the views which have been expressed‡ concerning the constitution of allylene, $CH-C-CH_3$, and propargylic ether $CH-C-CH_2.OC_2H_5$, the formation of the latter from allylene dibromide appears anomalous. Of the two possible formulæ for allylene $CH-C-CH_3$ and CH_2-C-CH_2, which correspond to its formation from dichloracetone chloride and sodium,§ the first is the more probable, considering that this body is a homologue of acetylene, and that only one atom of hydrogen in it is capable of being replaced by silver; but the formula $CH-C-CH_3.OC_2H_5$ for propargylic ether cannot be derived from any of the three formulæ for allylene dibromide $CHBr_2-C-CH_3$, $CH-CBr_2-CH_3$, $CHBr{=}CBr-CH_3$ corresponding to the formula $CH-C-CH_3$ for allylene. If, therefore, the probable formula $CH-C-CH_3$ for allylene be adhered to, the formula of propargylic ether can be changed into $CH-CH{=}CH.OC_2H_5$ or $CH-C(OC_2H_5){=}CH_2$, which would be isomeric with that before mentioned. Although the authors have not been able to prepare a sufficient quantity of the ether from allylene dibromide to thoroughly investigate the matter,

* Jahresb. f. Chem. 1865, 492.

† Ann. Ch. Pharm., clvi, 167.

‡ Ann. Ch. Pharm., cxxxv, 129.

§ Ann. Ch. Pharm., cxxxiii, 111.

they are of opinion that it is identical and not isomeric with propargylic ether.

Baeyer* supposed that the crystalline silver compound of propargylic ether was identical with the amorphous body produced by the action of ammonia on it. It is, however, a double salt of the formula $2(C_3H_2Ag.OC_2H_5) + AgNO_3$, the nitrate of silver of which is removed by treatment with ammonia. When an ammoniacal solution of silver chloride is added to an alcoholic solution of propargylic ether, a white curdy precipitate $2(C_3H_2Ag.OC_2H_5) + AgCl$. is obtained which is also decomposed, and the silver chloride removed, by prolonged washing with ammonia. An amorphous yellow copper compound $(C_3H_2.OC_2H_5)Cu_2$ is obtained by precipitating the ether with ammoniacal cuprous chloride. Cuprous chloride, without addition of ammonia also produces a precipitate which has not been examined. The formula for the copper compound (Cu = 63·4) shows that it is a cuprous compound, and that two molecules of the ether are held together by the copper atoms, $\begin{array}{l} C_3H_2-Cu-Cu-C_3H_2 \\ | \qquad\qquad\quad | \\ C_2H_5 \qquad\quad OC_2H_5 \end{array}$. This is the reason why cupric salts give no precipitate. From the similarity of the reaction of silver salts and cuprous chloride with acetylene, allylene, propargylic ether, &c., the authors infer that the formula of argento-propargylic ether is $\begin{array}{l} C_3H_2-Ag-Ag-C_3H_2 \\ | \qquad\qquad\quad | \\ O.C_2H_5 \qquad\quad OC_2H_5 \end{array}$ which is rendered probable by a comparison with the acetylene compound $C_4Br_3Ag_3 = 2(C_2BrAg) + AgBr$, described by Behrend,† and that observed by Berthelot‡ on passing allylene into ammoniacal silver chloride, $C_6H_6Ag_3Cl = 2(C_3H_3Ag) + AgCl$; and lastly, Glaser§ mentions a silver compound $2(AgC_2.C_6H_5) + Ag_2O$, which exactly corresponds to the copper compound $(C_2C_6H_5)_2Cu + CuO$.

Wislicenus‖ has very recently propounded the view that silver is diatomic, which would bring it into relation with copper and mercury, the elements to which it has such close chemical analogy, although the isomorphism of many silver salts with those of sodium and potassium is at variance with this. According to this view $\begin{array}{l} AgCl \\ | \\ AgCl \end{array}$ and $\begin{array}{l} AgNO_3 \\ | \\ AgNO_3 \end{array}$ are analogous to $\begin{array}{l} CuCl \\ | \\ CuCl \end{array}$, and allylene-silver and silver-propargylether are brought into agreement with these by the formulæ $\begin{array}{l} Ag.C_3H_3 \\ | \\ Ag.C_3H_3 \end{array}$ and

* Ann. Ch. Pharm., cxxxviii, 196.
† Ann. Ch. Pharm., cxxxv. 264.
‡ Bull. Soc. Chim. [2], v, 176, 413.
§ Zeits. f. Chem. 1869, 97.
‖ Deut. Chem. Ges. Ber., iv, 63.

$\begin{array}{l} Ag.C_3H_2.OC_2H_5 \\ | \\ Ag.C_3H_2.OC_2H_5 \end{array}$. The question remains open whether the structure of those double salts which contain no other metal than silver cannot be explained on the supposition that silver is bivalent. Wislicenus founds his argument on the existence of the double salt $AgNO_3AgI$, and Berthelot's silver-acetylene chloride $C_2HAg + AgCl$, which he considers to be $\begin{array}{l} AgNO_3 \\ | \\ AgI \end{array}$ and $\begin{array}{l} AgC_2H \\ | \\ AgCl \end{array}$. But several series of such compounds exist.

I. (AgX,AgY). — $AgNO_3,AgI$; $AgNO_3,AgBr$; $AgOH,AgFl$; $C_2HAg,AgCl$.

II. $2(AgX),AgY$. — (?) $2(AgNO_3)AgI$; $2AgCy,AgNO_3$; $2(C_3H_3Ag)AgCl$; $2(C_2BrAg)AgBr$; $2(C_3H_2Ag,OC_2H_5)AgNO_3$; $2(C_3H_2Ag,OC_2H_5)AgCl$.

III. $2(AgX),Ag_2O$.—$2(Ag_2CO_3) + Ag_2O$; $2(AgC_2C_6H_5) + Ag_2O$.

The structure of the first group can be explained without considering them as double salts, on the supposition that silver is diatomic; but this is not possible for the second series. It remains, therefore, either to consider all these compounds, the first as well as the second series, as double salts, or to seek an explanation of their structure in another atomicity of silver; but the specific heat of silver agrees with the atomic weight 108.

It is also against the hypothesis that silver (108) is triatomic, that we should then be unacquainted with any compounds which would contain a single atom of that element; and from what we know of silver peroxide it is scarcely likely that they could exist. There remains one other hypothesis, that the ordinary monatomic silver sometimes becomes triatomic. The above-mentioned compounds could then be easily explained:—

1. $AgNO_3$. 2. $IAg = AgNO_3$. 3. $C_3H_3Ag = AgC_3H_3$.

4. $\begin{array}{l} C_3H_3Ag - AgC_3H_3. \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad AgCl. \end{array}$ 5. $O\left\langle\begin{array}{l} Ag - AgC_2C_6H_5. \\ | \\ Ag - AgC_2.C_6H_5 \end{array}\right.$.

There is, however, a difficulty, inasmuch as the silver can be removed from such compounds as 3 and 4 by cautious oxidation. The authors are of opinion that this theory of the variable atomicity of silver should be employed with extreme caution; and they have come to the conclusion to accept with Wislicenus the diatomicity of silver, but also to regard the compounds mentioned as double salts.

Berthelot considered the metallic compounds of acetylene and allylene as containing peculiar silver and copper radicles, which he named cuprosoacetyl, Argentacetyl, &c., forming oxides, chlorides, and salts. The authors, however, do not agree with this view, since the hydro-

carbons, acetylene, and allylene are so easily evolved from these compounds by the action of acids. The ready decomposition also of the perfectly analogous silver nitrate, silver propargyl ether, and silver chloride, silver propargylether by ammonia, and the argentallyl oxide sulphate by water, and the change of the so-called argentallyl oxide into argentallylene, appears to point out that here there is only a loose combination, which can be more simply explained on the hypothesis of the polyvalence of the metals.

C. E. G.

On the Cresols of Coal-Tar. By H. L. Buff.*

The author has submitted commercial coal-tar creosote to fractional solution in soda-ley, and the resulting alkaline solutions to fractional precipitation with hydrochloric acid, in the hope of obtaining pure cresol, but fruitlessly. A fraction boiling constantly at 204°—205° was treated with chloride of benzoyl, by which means a solid compound and a liquid were produced. The solid body was obtained in large, white, hard crystals, which melted at 70°—70·5°, and solidified at 52·6°. Its properties agree with those of paracresyl benzoate, which melts at 70°. The cresol obtained from the solid ether was a colourless body, having a sharp urinous smell. It solidifies in a mixture of ammonium sulphocyanate and water, melts at 34°, and boils at 205°. Its properties are those of paracresol.

The liquid which was obtained in addition to the solid ether boils at above 360°, and does not solidify in a mixture of water and ammonium sulphocyanate. It is decomposed by boiling with alcoholic potash into benzoic acid and cresol. The cresol could not be obtained in a solid condition; fused with potash, it gave the reaction of salicylic acid with ferric chloride, from which it would not seem to be pure metacresol.

W. H. D.

On some Nitrogen Compounds of Anthraquinone. By Rud. Boettger and T. Petersen.†

It is well known that nitro-derivates cannot be obtained directly from anthraquinone by the action of nitric acid; by the oxidation of anthracene with nitric acid, however, there is obtained a dinitroanthraquinone, together with anthraquinone, identical with Anderson's binitrooxanthracene and Fritsche's oxobinitrophotene.

1. That the nitration of anthraquinone was readily effected by a mixture of concentrated sulphuric and nitric acids was known to Fritsche, and has since been confirmed by Liebermann and by one of

* Deut. Chem Ges. Ber. iv, 378. † Ber. Deut. Chem. Ges. iv, 226.

the authors. The body thus obtained, which the authors find is a true *dinitroanthraquinone*, separates, on pouring the acid mixture into water, in yellowish-white flocculi, insoluble in water, difficultly soluble in alcohol and benzene, still less soluble in ether, and crystallising from these solvents in minute monoclinic, almost colourless crystals. At about 252° it cakes together to a brown mass, from which, at higher temperatures, under partial decomposition of the residue, yellow to brown, needle-like crystals sublime. This body forms crystalline double compounds with various hydrocarbons, as already observed by Fritsche. It does not yield the fine violet compound with anthracene given by Fritsche's "reagent." On fusion with potassium hydrate, it yields alizarin in considerable quantity, a proof that the two nitro-groups occupy the same positions as the two OH groups do in alizarin.

2. Dinitroanthraquinone is easily reduced to *diamidoanthraquinone.** On warming it with a solution of sodium sulphydrate, the liquid first assumes a deep emerald-green colour, from which the amido-compound is soon deposited as a bright, vermillion-red powder, more or less soluble in alcohol, ether, acetic ether, and other solvents, readily soluble in acids, especially when concentrated. From dilute acid solutions it separates out gradually on standing, its basic properties being exceedingly weak. It melts at 236°, and sublimes even below this in magnificent garnet-red flat needles, with a greenish reflex, often united in feather-like groups. From alcohol and ether it crystallises in small needles. On fusion with potassium hydrate it yields alizarin in quantity.

3. The action of nitrous acid on a solution of diamidoanthraquinone in concentrated acid was without result; an azo-derivative was indeed formed, but it remained for the greater part in solution, and was decomposed with reproduction of anthraquinone by the continued action of nitrous acid. But by acting on an ethereal or acetic ether solution, peculiar azo-derivative was obtained. This body soon separates out, on passing a current of the gas through the liquid, as a delicate brownish-violet powder, extremely alterable, and decomposed with slight detonation at about 68°, a bulky residue of carbon remaining. Analyses of several preparations led to the formula $C_{14}H_8N_4O_4$. It is soluble in alcohol and water, with a beautiful violet colour. When heated or left to stand for some time, both the aqueous and alcoholic solutions are decomposed, and regenerated diamide falls down, together with a brown decomposition product, accompanied by but a slight evolution of nitrogen. The authors look upon this compound as a dinitrosoamido-

* The authors recommend two reducing agents for use in similar cases: *a*, a potash solution of stannous oxide; *b*, a solution of crystallised sodium sulphydrate, often to be preferred to ammonium sulphydrate.

anthraquinone, containing twice the univalent $N\left\{\begin{matrix}H\\NO\end{matrix}\right.$ group, or in accordance with Graebe and Ludwig's observations on certain naphthol derivatives, as a dioximidoamidoanthraquinone, containing twice the univalent group, $N\left\{\begin{matrix}HN\\O\end{matrix}\right\rangle$, and express the reaction by the equation:—

$$C_{14}H_6(NH_2)_2O_2 + 2HNO_2 = C_{14}H_6(N\left\{\begin{matrix}HN\\O\end{matrix}\right\rangle)_2O_2 + 2H_2O.$$

on treatment with potassium hydrate alizarin is formed.

4. Remarkable is the action of concentrated sulphuric acid on dinitro-anthraquinone. When it is dissolved in excess of acid (about 1 pt in 18 pts), and the mixture is heated on the sand-bath at about 200°, a moderate evolution of sulphurous anhydride takes place, the brown-yellow liquid becoming deep brown-red. On the reaction becoming more violent, the source of heat is removed, the whole being afterwards heated again slowly, until the evolution of sulphurous anhydride ceases. The mass is then poured into cold water; the precipitated dark brown-red flocculi are well washed, repeatedly dissolved in dilute alkali, reprecipitated by acid, and finally dissolved in alcohol; and the solution is slowly evaporated. The exceedingly stable new colouring matter, which can also be obtained by treating anthraquinone with a mixture of sulphuric and nitric acids (16 to 18 parts conc. sulphuric and 1 part nitric acid, sp. gr. 1·5), is slightly soluble in water, forming a peach-coloured solution; readily soluble in alcohol, ether, acetic ether, and chloroform, less soluble in benzene, with a magnificent red violet colour. It separates from these solvents, on slow evaporation, in a violet-red crystalline-granular form; on quick evaporation, in violet-brown, metallic glistening crusts. Cotton is dyed violet by it without the use of mordants. On heating, it melts, but only a small portion sublimes unchanged. Analysis leads to the formula $C_{14}H_8N_2O_4$. On fusion with potassium hydrate, ammonia is evolved, but no alizarin could be detected. On treatment with zinc and sulphuric acid, gradual decolorisation and decomposition took place.

H. E. A.

Note on the Communication of Boettger and Petersen, on some Nitrogen Compounds of Anthraquinone. By C. LIEBERMANN.*

THE author briefly relates his observations on dinitroanthraquinone (from anthraquinone) which he has long been engaged in investigating in the same direction as Boettger and Petersen. He finds dinitro-

* Deut. Chem. Ges. Ber., iv, 230.

anthraquinone to be easily reduced by tin and hydrochloric acid, the product, on boiling the resulting mass with water, separates in the form of a red power, which has the composition of diamidoanthraquinone. It is soluble only in concentrated acids, crystallises well from benzene, and sublimes in long hair-fine needles. Heated with concentrated sulphuric acid, it yields no colouring matter, a fact of importance in connection with the determination of the course of the reaction in the formation of naphthazarin. On fusion with potassium hydrate, a blue solution is obtained; the colouring matter thus formed, which Boettger and Petersen consider to be alizarin, exhibits, when isolated, certain differences, particularly on sublimation and on exposure of its solution in potash to the air, which caused the author to doubt the identity of the two bodies. The same compound is formed by fusing the product of the action of nitrous acid on diamidoanthraquinone with potassium hydrate; on the other hand, on heating with aqueous potash, a yellow solution is obtained, so that only a partial conversion of the NH_2 groups by the nitrous acid must be looked upon as having taken place.

The colouring matter produced by the action of sulphuric acid on dinitroanthraquinone, in the form of a black non-crystalline powder, was not analysed by the author, as he believed the condition in which it was obtained did not offer a sufficient guarantee of its purity. He finds that on heating with water to 200°, it is converted into a spongy aggregate of dark crystalline needles, which may be sublimed, but with considerable loss by carbonization. Metallic-green shining needles are thus obtained, in many respects much like naphthazarin. These contain nitrogen, although it would seem in no very considerable quantity. The vapour of this body strikingly resembles that of indigo.

H. E. A.

On some Derivatives of Anthraquinone. By TH. PETERSEN.*

R. BOETTGER and the author investigated a short time ago a *dinitroanthraquinone*, which as Fritsche has found, is formed by treating anthraquinone with a mixture of concentrated nitric and sulphuric acid. This body yields, on fusion with caustic potash, large quantities of alizarin, and is therefore isomeric with Anderson's binitro-oxanthracene, which gives with caustic potash a body dissolving in alkalis with a reddish brown colour.

The violet body, formed by treating dinitroanthraquinone with concentrated sulphuric acid, is *di-imido-hydroxyl-anthraquinone*, $C_{14}H_8N_2O_4$. On passing nitrous acid into its solution in alcohol and ether, *oximido-dihydroxyl-anthraquinone* $C_{14}H_7NO_5$ is formed, which by sublimation is obtained in yellow or hyacinth-red, flat, feathery needles, which dissolve

* Deut. Chem. Ges. Ber. iv, 301.

in caustic alkalies with a raspberry colour, and when fused with caustic potash, give alizarin. When this body is dissolved in concentrated nitric acid, *dinitro-dihydroxyl-anthraquinone* is obtained, which, by the addition of water, separates in yellow, very electric flakes, dissolving in caustic potash with a violet colour.

The formation of the oximido-compound corresponds to that of oximido-α-napthol which Graebe and Ludwig obtained by the same reaction from di-imodo-α-naphthol.

C. S.

On a By-product in the Manufacture of Alizarin.
By C. Liebermann.*

The products obtained by melting anthraquinone-sulphonic acid with potash, differ according to the manner in which the process is conducted. If the action of the alkali is energetic, alizarin and monoxyanthraquinone-sulphonic acid are formed; but if the action is rendered less intense by admixture of chalk, a completely different body is obtained, the most remarkable property of which is, that on melting with pure alkalies it is changed into alizarin.† It can be separated easily from alizarin by its solubility in baryta-water, and is precipitated again by hydrochloric acid; when purified by sublimation and by crystallisation from acetic acid, it is obtained in yellow needles. It dissolves in alkalies with red-brown colour, but does not give colours with mordants; with lead-acetate it forms a bright yellow precipitate.

In its properties it closely resembles Rochleder's isoalizarin; the analysis of the new body shows, however, that it is monoxyanthraquinone, $C_{14}H_7{}^{O_2}_{OH}$; the change into alizarin by melting with potash is by oxidation, $C_{14}H_7{}^{O_2}_{OH} + O = C_{14}H_6{}^{O_2}_{(OH)_2}$. This reaction is explained by the fact that monobromanthraquinone, on melting with potash, passes into the dioxy-derivative.

Whether the described substance is derived from pure disulphanthraquinonic acid, or from a mixture of this acid with the monosulphoacid, is not yet proved. Some experiments tend towards the former conclusion. This is not impossible, for in every melting for alizarin, a little anthraquinone is reproduced.

A. P.

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* Deut. Chem. Ges. Ber., iv, 103.

† The same substance has been described by Schunk under the name of *anthraflavic acid.* See p. 380 of this volume.

On Benzoïn. By LIMPRICHT and SCHWANERT.*

ONE of the authors of this paper, in conjunction with Jena, has already shown† that when benzoïn is heated with alcoholic potash, benzilic acid is formed, but in so small a quantity that it was ascribed to benzil present as an impurity in the benzoïn employed. The authors however find that under certain circumstances benzil is formed by the action of alcoholic potash on pure benzoïn: for when these are heated in an open flask, the solution shows, even from the first, the dark violet colour so characteristic of benzil. If water be added to the solution after some hours' digestion, a mixture of various substances is precipitated, amongst which are toluylene alcohol (orthorhombic) and *benzil.* Two hundred grams of benzoïn quite free from benzil yielded, by this process, several grams of benzil. That this is produced by the oxidising action of the atmosphere, is shown by the circumstance, that when the air is excluded by conducting the operation on sealed tubes, benzil is not formed, and the violet colour at first apparent quickly disappears when the tubes are heated.

The addition of hydrochloric acid to the filtrate from the precipitate produced by adding water to the alcoholic solution, separates benzoic acid, benzilic acid (3—4 grms. from 200 of benzoïn), and a third compound, the so-called tolane alcohol, which Jena obtained in minute quantity in the conversion of benzil into benzilic acid.‡ The authors find, however, that it is derived from the benzoïn which must have been present as an impurity in the benzil employed by Jena. On boiling the hydrochloric acid precipitate with water, the benzoic acid and benzilic acid dissolve, leaving behind a resinous body, Jena's tolane alcohol ($C_{14}H_{12}O_2$), which, however, according to the authors, has the composition $C_{30}H_{26}O_4$, and is therefore *ethyldibenzoin.* It crystallises well from its alcoholic solution, and fuses at 200°.

Whilst, in the formation of benzil, one molecule of benzoïn loses two atoms of hydrogen, in the formation of ethyl-dibenzoïn two molecules of benzoïn lose two atoms of hydrogen, and unite to form one molecule of dibenzoïn, in which one atom of hydrogen is replaced by ethyl.

$$\text{Benzoïn} \left\{ \begin{array}{l} C(C_6H_5)_2HO \\ COH \end{array} \right. \qquad \text{Ethyl-dibenzoïn} \left\{ \begin{array}{l} C(C_6H_5)_2C_2H_5O \\ CO \\ CO \\ C(C_6H_5)_2HO. \end{array} \right.$$

By heating with acetyl chloride, acetylethyl-dibenzoin,

* Deut. Chem. Ges. Ber., iv, 335—338.

† Ann. Ch. Pharm., clv, 89.

‡ Deut. Chem. Ges. Ber., ii, 384, and Ann. Ch. Pharm., clv, 80.

$$\left\{\begin{array}{l} C(C_6H_5)_2C_2H_5O \\ CO \\ CO \\ C(C_6H_5)_2(C_2H_3O)O \end{array}\right.$$

is formed. It is a crystalline compound, and melts at 145°.

Ethyl-dibenzoïn is not obtained when benzoïn is heated with alcoholic potash in sealed tubes, hydrochloric acid precipitating from the solution, benzoic acid, traces of benzilic acid, and the uncrystallisable ethyl-benzilic acid, $C_{14}H_{11}(C_2H_5)O_3$.* There are at present three compounds known which are derived from two molecules of benzoïn by the action of alcoholic potash, viz.,

$$C_{28}H_{22}O_3\dagger \quad \left\{\begin{array}{l} C(C_6H_5)_2HO \\ CO \\ C(C_6H_5)_2 \\ COH \end{array}\right. \qquad C_{28}H_{26}O_2\dagger \quad \left\{\begin{array}{l} C(C_6H_5)_2HO \\ CH_2 \\ CH_2 \\ C(C_6H_5)_2HO \end{array}\right. \qquad C_{30}H_{26}O_4 \quad \left\{\begin{array}{l} C(C_6H_5)_2C_2H_5O \\ CO \\ CO \\ C(C_6H_5)_2HO. \end{array}\right.$$

A fourth compound, closely allied to these, is oxylepidin, which Zinin obtained by the action of hydrochloric acid upon benzoïn.‡ The authors have observed that dilute sulphuric acid produces the same effect:

$$2(C_{14}H_{12}O_2) - 2H_2O = C_{28}H_{20}O_2.$$

Oxylepidin is closely allied to the compound $C_{28}H_{22}O_3$, and would undoubtedly be obtained from it by the action of acids. The authors find that when a mixture of oxylepidin and benzoin is heated with water to 150°, these bodies are converted into lepidin, $C_{28}H_{20}O$, and benzil, respectively. This would account for the results obtained by Zinin, who found the two latter to be the chief products of the action of hydrochloric acid on benzoin.

C. E. G.

On the Decomposition of Acroleïn-ammonia by Dry Distillation.
By Ad. Claus.§

Baeyer, in his experiments on the synthesis of the pyridine bases|| has found that picoline occurs as a product of the destructive distillation of acroleïn-ammonia, and this determined the author to ascertain whether the base, formerly obtained by him,¶ was really picoline or not. For this purpose he recrystallised, from boiling water, some of the platinochloride of the base which he had prepared during his previous research, and obtained the prismatic crystals containing 3·1

* Ann. Ch. Pharm., clv, 100.
† Ann. Ch. Pharm., clv, 100.
‡ Chem. Centrabl. 1867, 373.
§ Ann. Ch. Pharm., clviii, 222—230.
|| Ann. Ch. Pharm., clv, 285.
¶ Ann. Ch. Pharm., cxxx, 185.

per cent. of water of crystallisation described by Baeyer. By long boiling with water, also, the characteristic bright yellow pulverulent precipitate mentioned by him was formed. In the author's former experiments he had recrystallised the platinum salt by dissolving it in warm water and precipitating by alcohol, thus obtaining a salt which was anhydrous and had a different crystalline form. This would account for the apparent discrepancy between his results and those of Baeyer. Professor Werber has also compared the toxicological action of this base with the picoline from bone-oil, and finds that they agree completely in their physiological action.

The author, in his previous experiments, had submitted the crude product obtained by the decomposition of acroleïn-ammonia to fractional distillation, and separated it into two portions, one of which came over between 100° and 150°, the other between 150° and 200°. The latter, even after repeated rectification, always began to boil at about 120°, the temperature gradually rising to 200°. The platinum salts, moreover, of the different fractions agreed in form and composition. From these results he concluded that the base under examination could not be distilled without decomposition, but that the portion which came over first, between 120° and 150°, was the nearly pure substance.

In order to investigate this subject, the author has recently prepared a fresh quantity of the oil by the dry distillation of acrolein-ammonia. He first endeavoured to effect a separation by agitating the crude product with water, but found that, with the exception of a little tarry matter, it was completely soluble in about 100 volumes of that fluid. The solution was therefore neutralized with hydrochloric acid, filtered and evaporated at 100°, when the peculiarly offensive odour so characteristic of the acroleïn-compounds became apparent. The concentrated solution was filtered and agitated with ether, after an excess of caustic potash had been added to it. The ethereal solution was then dried by calcium chloride and evaporated, thus obtaining the basic products in a pure state. These can be easily separated by adding platinum tetrachloride to a dilute solution of their hydrochlorides, the picoline double salt then remains dissolved, whilst the platinum salt of the other base is precipitated. This simple method of separation, however, was not discovered before the greater portion of the purified bases had been submitted to fractional distillation. In order to remove the picoline, the mixture of the bases was slowly and cautiously heated to 150°, when about one-third came over, which was used for the physiological experiments. The residue, after it had become quite cold, was again heated to 140°, but nearly pure picoline began to come over at 120°. This operation was repeated upon the residue three times with the same result, and, to confirm the results formerly obtained, a small

portion of this residue was decomposed by repeated distillation into picoline and tarry and carbonaceous substances; the larger portion, however, was treated with hydrochloric acid, which left undissolved a considerable quantity of resinous products. The largely diluted dark brown solution gave with platinum tetrachloride a brown curdy precipitate, and, on evaporating the pale yellow mother-liquor, a considerable quantity of the picoline platinochloride was obtained. The brown precipitate was purified by washing first with warm water and finally with alcohol, when it was found to contain 31·3 per cent. of platinum, which exactly corresponds to acroleïn-ammonia. It would appear that this platinum salt is decomposed by boiling with water, forming the picoline platinum salt. By boiling the powdered salt with water, it was changed into a dark red mass resembling coagulated albumin, and then contained 31·5 to 31·6 per cent. of platinum. The filtrate, on cooling, deposited first an indistinctly crystalline yellow curdy platinum salt, containing 32·2 to 32·3 per cent. platinum, and afterwards the picoline platinum salt. If this curdy platinum salt (with 32·2 per cent. Pt.) was again boiled with water it underwent the same change as the original salt, and left as a residue a bright yellow, hard brittle mass, still giving 32·2 per cent. platinum; this, as well as the original residue (with 31·5 to 31·6 per cent. Pt.), could now be boiled with water without undergoing any change.

From these results the author concludes that the base which is decomposed by distillation approaches in composition more nearly to acroleïn-ammonia than to picoline, and is either isomeric with it (C_6H_9NO), or is an intermediate product between it and picoline (C_6H_7N). From the fact that this base is decomposed by distillation, yielding picoline and tarry products it is extremely probable that the picoline obtained in the destructive distillation of acroleïn-ammonia does not arise directly from its decomposition, but rather from that of the non-volatile base. This accords with the fact that when the acroleïn-ammonia is slowly heated, the distillate contains a larger proportion of picoline than when the distillation is more rapidly conducted.

C. E. G.

On some Derivatives of Deoxybenzoïn. By N. Zinin.*

Deoxybenzoin is not acted upon by alcoholic potash-solution when the air is carefully excluded; if however, the air has access, needle-like crystals are gradually deposited. To prepare these, a mixture of 100 grms. deoxybenzoin with 100 grms. potassium hydrate dissolved in 1 litre of 90 per cent. alcohol is left at rest; in this way about

* Zeitschr. f. Chem. [2], vii, 127; from Petersb. Acad. Bull. xvi, 340.

20 grms. of the crystals were formed in 14 days. The solution finally contains potassium benzoate only. The body thus formed, $C_{70}H_{56}O_4$ *Benzamarone*, melts at 225°; is soluble in 157 parts of boiling, and 1,130 parts of cold 97 per cent. alcohol; in 10 parts of boiling benzene and 35 parts of boiling acetic acid. On long heating with alcoholic potash, benzamarone yields deoxybenzoin and amarinic acid in about equal proportions; first unaltered benzamarone is deposited, then on the addition of water, deoxybenzoin; and finally after evaporation, potassium amarinate, the latter in the form of an oil which solidifies on cooling in white scales insoluble in the excess of potash. *Amarinic* acid, $C_{42}H_{42}O_7$, is thrown down by all acids, even acetic, in the form of a white, curdy, crystalline precipitate, insoluble in cold water, but soluble in boiling alcohol, ether and acetic acid. It loses 1 mol. water at 125°, and melts at 140°, losing a further $1\frac{1}{2}$ mol. of water, and then solidifies in the crystalline form. Acid once heated to 140° melts at 155°, is no longer soluble in 15 parts 90 per cent. acohol, dissolves in ammonia at 110°—120°, also in potash-solution, forming potassium amarinate, Potassium amarinate, $C_{42}H_{40}K_2O_7$ + aq. is obtained from boiling ether, either in lamellæ, or as an oil gradually solidifying in warty groups. The barium, lead, and silver salts are curdy, loose, amorphous precipitates, which gradually become heavy and crystalline. The silver salt, $C_{42}H_{38}Ag_2O_6$, is white, and almost insoluble in water and alcohol. The barium salt crystallises well from alcohol. All the salts are bitter.

H. E. A.

On Saliretin. By K. Kraut.*

The author prepares saliretin as follows. Triturated saligenin is agitated with 10 parts of hydrochloric acid of sp. gr. 1·125 till it dissolves, and the solution is heated to 80°; the liquid, which has become pulpy from separation of saliretin, is poured into a large quantity of water; the precipitated and washed saliretin is dissolved in moderately strong spirit; and the solution, filtered from a gelatinous body, is poured into a large quantity of solution of salt, which precipitates the saliretin in curdy flocks. The product is a yellowish or reddish-yellow powder, which runs together and turns brown at 200°, without losing weight. It dissolves almost entirely in absolute alcohol. But when saligenin is decomposed by hydrochloric acid at a temperature not exceeding 40°, a solution of the product in weaker spirit gives, on addition of absolute alcohol, a precipitate, which, however, does not differ from saliretin in composition and properties. The author, from his own and Piria's analyses, deduces for saliretin the formula $C_{14}O_{14}O_3$, already proposed by

* Zeitschr. f. Chem. [2], vii, 92, from Ann. Chem. Pharm., clvi, 123.

Moitessier (*Jahresbericht*, 1866, 677), and hence regards it as saligenosaligenin, $HO.C_6H_4.CH_2.O.C_6H_4.CH_2.OH$. Saligenin is not converted by potassium permanganate into salicylic aldehyde, salicylic acid, or any well-characterised body.

A saliretin prepared by Gerhardt (*Ann. Chem. Phys.* [3] 7, 215) by the action of sulphuric acid is regarded by the author as trisaligenosaligenin, $C_{28}H_{26}O_5$: the resinous product obtained by Beilstein and Seelheim (*Ann. Ch. Pharm.* cxvii, 83) by the action of acetic anhydride or ethyl iodide on saligenin is regarded by him as heptasaligenosaligenin, $C_{56}H_{50}O_9$.

J. R.

Hæmatoxylin. By Franz Reun.*

The investigations of hæmatoxylin hitherto published† have established only the empirical formula of this substance, which when dried at 130°, Gerhardt gives as $C_{16}H_{14}O_6$, and the hæmatein formed by its oxidation in alkaline solutions as $C_{16}H_{12}O_6$. Hæmatoxylin is sweet, yields oxalic acid by oxidation, and cannot be nitrated. Chlorine and bromine convert it into resinous products: sodium amalgam, and zinc and sulphuric acid are without action on it. Phosphoric chloride acts upon it, but nothing could be obtained from the product of the reaction, either by distillation or treatment with ether. Potassium chlorate and hydrochloric acid yield an amorphous resinous product.

The action of ammonia forms Erdmann's hæmatein, and if long continued, humus-like substances. Hydriodic and hydrobromic acids yield resinous products which cannot be purified; and by heating with zinc powder, a crystalline substance was obtained, but in far too small a quantity to enable the author to investigate it. He has, however, discovered three reactions by which crystalline substances are produced from hæmatoxylin, which establish the number of hydroxyl groups it contains and the class of compounds to which it belongs.

1. When hæmatoxylin is treated with acetyl chloride, hydrochloric acid is evolved; and if, when the reaction is ended, the product be evaporated on the water-bath, the pale yellow syrupy mass poured into water, and the white flocks which separate, be collected, well washed, and dissolved in alcohol or acetic acid by the aid of a gentle heat, the concentrated solution will solidify on cooling to a pulp of extremely slender lustrous needles. As the substance is rapidly altered by contact with the air, all the operations must be conducted as rapidly as possible. The air-dried substance contains no water of crystallisation, and can be heated to 100° without decomposition. The analysis

* Deut. Chem. Ges. Ber., iv, 329.

† Erdmann, J. (pr. Chem. xxv. 193, and lxxv, 218); Hesse. (Ann. Ch. Pharm. cix, 332).

agrees with the formula $C_{16}H_8(C_2H_3O)_6O_6$, in which six atoms of the hydrogen in the hæmatoxylin, are replaced by six acetyl groups; all the oxygen in the hæmatoxylin is, therefore, present as hydroxyl. A similar substitution-product is obtained by the action of benzoyl chloride, but it is resinous and difficult to purify.

2. If a few drops of concentrated sulphuric acid be added to an ethereal solution of hæmatoxylin (1 : 50), and the solution allowed to stand, it gradually becomes dark-coloured, and after some time, brownish red crystals are deposited on the sides of the vessel. These are collected and washed with ether until it runs off colourless. The compound is only slightly soluble in cold water, but more so in hot water, forming a brownish-red solution which solidifies on cooling to a gelatinous mass, and on the evaporation of the water, this leaves amorphous scales having a cantharides-green lustre. It cannot be recrystallised from alcohol. Ammonia and the other alkalies colour it a fine violet blue. This substance is identical with Erdmann's hæmatein, which has not, hitherto, been obtained in the crystalline state. Analysis showed the composition of the green scales, dried in the air, to be $C_{16}H_{12}O_6 + 3H_2O$; the crystals dried over sulphuric acid $C_{16}H_{12}O_6 + H_2O$, and the same dried at 100°, $C_{16}H_{12}O_6$. The method of preparation here described shows that the formation of hæmatein by the action of ammonia and air on hæmatoxylin, as given by Erdmann, is only an effect of oxidation. Hæmatein can easily be reconverted into hæmatoxylin by boiling its aqueous solution with zinc and sulphuric acid, or preferably, sulphurous acid, until it becomes colourless, and then extracting the hæmatoxylin by agitation with ether.

3 Hæmatoxylin is fused with potassium hydrate (1 : 4) until it acquires a brown colour, and the product, after being neutralised with dilute sulphuric acid and filtered, is agitated with ether. The ethereal solution leaves on evaporation a syrupy residue, and this, when submitted to distillation, yields a crystalline substance which can readily be identified as pyrogallic acid, $C_6H_6O_3$.

From these results the author draws the following conclusions:—

(1.) That hæmatoxylin has not the constitution of the saccharine substances resembling phloroglucin. (2.) That it is a derivative of the aromatic series. (3.) That it resembles hydroquinone in its behaviour towards weak oxidising agents, hæmatein having the same relation to hæmatoxylin, that quinone has to hydroquinone. (4.) That it contains six hydroxyl groups.

The subjoined may be taken as a shortened expression for the constitution of these compounds:—

$$\text{Hæmatoxylin} \begin{cases} C_6H_2(OH)_3 \\ C_4H_4 \\ C_6H_2(OH)_3 \end{cases} \qquad \text{Hæmatein} \begin{cases} C_6H_2(OH.)_2O \\ C_4 \\ C_6H_2(OH.)_2O. \end{cases}$$

From this it can readily be seen how pyrogallic acid is formed from hæmatoxylin.

The substance having the closest relation to hæmatoxylin is brasilin $C_{22}H_{20}O_7$. The difference in the formulæ of these two compounds is C_6H_6O; and Bolley* found that when brasilin was treated with nitric acid it yielded a yellow acid which he considered to be picric acid, but which, from its properties, appears to be styphnic acid. It is probable that brasilin is a derivative of hæmatoxylin in which the groups C_6H_5 and HO are contained, and the author has already obtained a crystalline *brasilein* by a process similar to that by which he obtained hæmatein.

C. E. G.

On Starch and Cellulose. By F. A. Flückiger.†

The author having obtained a fresh supply of lerp-manna resumed his former researches on this substance. Lerp-manna occurs on the leaves of "*Eucalyptus dumosa*," and consists of white threads clotted together by a syrup proceeding from the insect (*Psylla Eucalypti*) which spins those threads. It consists in round numbers of water 14 parts, threadlike portion 33 parts, sugar 53 parts. The threads possess many of the most characteristic properties of starch, from which however they are sharply distinguished by their form. When lerp is washed with water the sugar dissolves and the threads swell but slightly, but dissolve to a slight extent, so that the solution is coloured blue by iodine. The threads freed from sugar by washing consist of a substance called by the author *Lerp-amylum.*

Lerp-amylum is very slightly soluble in cold water, not perceptibly more so in water at 100°, but entirely soluble to a thin transparent liquid when heated to 135° in sealed tubes with 30 parts of water—this solution on cooling deposits the original substance in flocks, without forming a jelly at any time. The separation is almost complete.

If the material employed in this experiment were originally free from sugar, the liquid left after the separation of the flocks will also be sugar-free. The flocks deposited from solution are insoluble in boiling water—therefore lerp-amylum suffers no chemical change on being heated to 150° with water. Heated in the air-bath to 190° while dry, it turns brown and is afterwards reduced only by solutions of iodine; at the same time it becomes partly soluble in hot water; hence it appears that lerp-amylum undergoes a change similar to that which occurs when starch is converted into dextrin. By oxidation with nitric acid, it yields oxalic acid but no mucic acid; it is neutral to vegetable colours, and is not precipitated by lead acetate, and is therefore not to be confounded with the gums, &c.

* J. pr. Chem. xciii, 351. † Arch. Pharm. [2], cxlvi, 7—31.

Ultimate analysis gave

	Calculated.	Found.	
C_{12}.....	44·4	43·7	43·07
H_{20}.....	6·2	6·6	6·4
O_{10}.....	—	—	—

Like starch, lerp-amylum rotates the plane of polarisation to the right; also on digestion with dilute sulphuric acid, &c., it forms a crystallisable sugar which agrees in its properties with dextrine. It is insoluble in ammonia cuprate and is homogeneous.

Though the behaviour of lerp-amylum to iodine and to water, and its insolubility in cuprammonia distinguishes it from cellulose, it is to be borne in mind that there are forms or conditions of cellulose which are blued by iodine and dissolve in water.

As it appeared that lerp-amylum constitutes a perfectly homogenous substance analogous to starch, the author considered it advisable to examine into the truth of the statements made by so many writers "that the granules of starch have coatings of cellulose," since the evidence on which that statement was made did not appear to him to be conclusive. According to the best authorities, cellulose is characterized by—insolubility in water—solubility in cuprammonia—and inability to form a coloured compound with iodine directly, *i.e.*, with iodine in absence of acids or salts; and it is stated that when starch is treated with saliva, pancreatic juice, pepsin, &c., the granulose is dissolved and the cellulose having the above properties is left. The author cannot confirm these statements, but shows that saliva, for instance, when employed in insufficient quantity, dissolves a portion of the starch, with production of such an alteration of the properties of even the dissolved part, that iodine no longer causes the production of a blue colour, and that the portion left undissolved is therefore probably only starch so far changed as to have lost the power of forming a coloured iodine compound. He found further that when starch is digested at 100°, with ten times its weight of glycerin diluted with an equal quantity of water, a large portion dissolves to a liquid which is sufficiently thin to allow that which remains undissolved to be separated by filtration, and to be subsequently thoroughly washed out with hot water without forming a paste. This undissolved fraction, which, if not pure cellulose, should at least contain a very much larger proportion of that body than the original material, takes a pure blue colour throughout its mass when treated with iodine in *aqueous* solution, and does not yield more of its substance to ammonic cuprate than does unaltered starch; and what small portion is dissolved cannot be reprecipitated by addition of an acid. He therefore concludes that it is not established that starch-granules contain cellulose. As the paper is mostly argu-

mentative, an abstract can give but a very incomplete idea of its value. C. H. G.

On the Products of the Acid Fermentation of Wheat Bran.

By August Freund.*

The author endeavoured to prepare propionic acid according to the method recommended by Keller (*Ann. Ch. Parm.*, lxxiii, 205), viz., an acid fermentation of wheat bran. He obtained however as the principal product, an oily substance, the formation of which is mentioned neither by Keller nor by Förster, who also followed out Keller's method for the production of propionic acid, but obtained formic acid as the principal product of the reaction. The author made two experiments, each on 1·26 kilograms of bran. In the one case 315 grams of tanned leather cuttings were employed as ferment; in the other, a similar quantity of hide which had been simply freed from fat by lime and not tanned. About $\frac{1}{2}$ a kilogram of chalk and 12·6 kilograms of water were added to each. The results in both cases were similar. The author finds that formic, acetic, butyric, and caproic acids are the ultimate results of the fermentation; a careful search for propionic and valerianic acids gave a negative result.

The author has prepared two hitherto undescribed compounds of caproic acid, the copper and zinc salts.

Caproate of Zinc is obtained by acting upon acetate of zinc with caproic acid, as a difficultly soluble crystalline precipitate. The precipitate redissolves partly on warming in the mother-liquor, and is deposited in small plates on cooling; the crystals separated from the mother-liquor are but slightly soluble in water, but readily soluble in warm alcohol, from which the salt separates in anhydrous crystalline needles having a mother-of-pearl lustre and a soapy feel. The formation of this salt may be employed as a method of distinguishing caproic acid from valerianic and butyric acid, neither of which forms a precipitate when added to an aqueous solution of zinc acetate. The same salt is produced by acting on oxide of zinc with an alcoholic solution of caproic acid.

Caproate of Copper.—Caproic acid precipitates from acetate of copper bluish-green heavy oily drops, which after a short time become crystalline. The salt is nearly insoluble in water, and may therefore be readily obtained pure by washing; it is readily soluble in alcohol and is obtained by spontaneous evaporation in small dark green anhydrous rhombohedrons.

The author has convinced himself by sundry experiments that the formation of the fatty acids in this fermentation is always preceded by

* J. pr. Chem. [2], iii, 224.

the formation of lactic acid, exactly as in the case of the formation of butyric acid from sugar.

E. T. C.

On the Formation of Lactic Acid from Sugar without Fermentation. By F. HOPPE-SEYLER.*

WHEN one pound of grape-sugar is placed in a capacious retort with $\frac{1}{2}$ litre of soda-solution of 1·34 sp. gr. and an equal quantity of water, and heated in a water-bath, violent action sets in at 96°, and the temperature rises to 116°, the liquid boiling violently. After cooling, the liquid is neutralized with dilute sulphuric acid and evaporated. On shaking with ether, lactic acid, a little oxyphenic acid, and other bodies dissolve. The ether is shaken with barium carbonate, and water; and the barium salt is then changed into a zinc salt, and recrystallised a few times, whereby it is obtained perfectly pure. From the percentage of water of crystallisation in the zinc salt, and from the solubilities of the zinc and calcium salts, the acid must be the normal lactic acid or ethylidene-lactic acid. A concentrated aqueous solution of the acid does not show circular polarization.

Lactic acid and calcium lactate are unchanged by water at 200°; neither is lactic acid produced by the action of water on sugar or paper at 200°.

A. P.

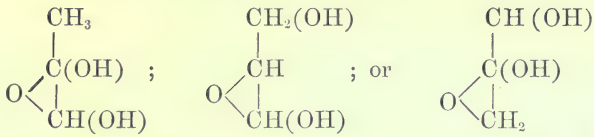
On Sarcolactic Acid. By E. ERLENMEYER.†

THE statements of different chemists respecting this acid are not quite accordant. Dosios (Ann. Ch. Pharm. cxlvi, 108) found that it is oxidised to malonic acid by the action of a mixture of potassium chromate and nitric acid, or of nitric acid alone. According to Erlenmeyer, however, malonic acid is not formed under these circumstances. According to Engelhardt (ibid. lxv, 363) the zinc-salt of sarcolactic acid dissolves in 2·23 pts. of alcohol, either cold or boiling. Erlenmeyer, on the contrary, finds that it is much less soluble in alcohol than in water. According to Wislicenus (Deut. Chem. Ges. Ber., ii, 620) the same salt is resolved, by addition of strong alcohol to its warm concentrated aqueous solution, into a sparingly soluble crystalline salt, which separates out, and an amorphous salt which remains in solution; but Erlenmeyer, on repeating this experiment, finds that the alcoholic mother-liquor of the crystalline salt crystallises to the very last drop.

All these differences may be explained by supposing that sarcolactic acid *sometimes* contains two isomeric lactic acids, but not always.

Erlenmeyer considers that besides the two well-known formulæ of α and β lactic acids, the following are possible expressions of the structure of acids of the formula $C_3H_6O_3$.

* Deut. Chem. Ges. Ber., iv, 346. † Ann. Ch. Pharm., clviii, 262—264.



C. R. A. W.

On the Basicity of Gluconic and Lactonic Acids. By H. HLASIWETZ.*

FITTIG† considers glucose to be the aldehyde of a hepta-acid alcohol, $C_6H_7(OH)_7$ derived from the saturated hydrocarbon C_6H_{14}, and hence to have the formula $C_6H_7\left\{\begin{matrix}O\\(OH)_5\end{matrix}\right.$; or in full

$$CH_2(OH)—CH(OH)—CH(OH)—CH(OH)—CH(OH)—CHO.$$

Like all aldehydes it should by oxidation yield an acid containing one atom of oxygen more, and differing in constitution only in that the last group CHO, becomes the group CO(OH): he considers gluconic acid accordingly to have this structure, viz:—

$$CH_2(OH)—CH(OH)—CH(OH)—CH(OH)—CH(OH)—CO(OH)$$

in accordance with which view it should be *monobasic.*

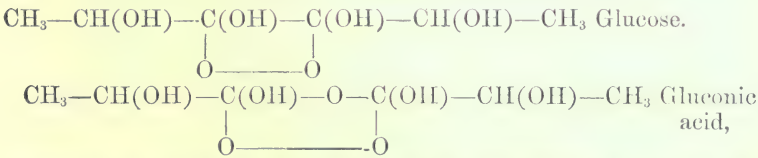
Hlasiwetz has prepared both a barium and a calcium salt wherein two atoms of hydrogen are replaced by the metal; and hence considers gluconic acid to be *bibasic.*

Similarly lactonic acid, which, according to Fittig's views, must also be monobasic, being derived from an isomeride of gluconic acid by abstraction of H_2O, is found to be really a bibasic acid, by the formation of calcium and barium salts wherein H_2 is replaced by the metal.

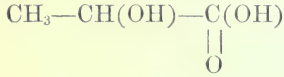
Hlasiwetz attributes to glucose this structure:—

$$CH_2(OH)—CH(OH)—C(OH)—C(OH)—CH(OH)—CH_2(OH)$$

but admits, from Hoppe-Seyler's recent production of β-lactic acid from glucose by the action of soda-ley,‡ that the following structures may be ascribed respectively to glucose and gluconic acid:—



glucose being, according to this view, a simple polymeride of β-lactic acid



C. R. A. W.

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* Ann. Ch. Pharm., clviii, 253—260.

† "Ueber die Constitution der sogenannten Kohlehydrate"; Tübingen, 1871.

‡ Deut. Chem. Ges. Ber., 1871, 346.

Solubility of Oxalates of the Alkali-Metals in water at Ordinary Temperatures. By W. R. NICHOLS.*

The following table contains the results of the author's observations:—

	Temperature.	Quantity of Salt in 100 pts. of saturated solution.	Quantity of Salt in 100 pts. water.	1 pt. Salt dissolves in
Oxalic acid:				
$C_2O_4H_2$	14°·5	8·73	9·56	10·46
Sodium salts:				
$C_2O_4Na_2$	13°	3·06	3·16	31·60
$C_2O_4HNa + H_2O$	10°	1·45	1·48	67·57
Potassium salts:				
$C_2O_4K_2 + H_2O$	16°	24·81	32·99	3 03
$C_2O_4HK + \frac{1}{2}H_2O$	18°	3·68	3·82	26·21
$C_2O_4HK.C_2O_4H_2 + 2H_2O$	13°	1·78	1·81	55·25
Ammonium salts:				
$C_2O_4(NH_4)_2 + H_2O$	15°	4·05	4·22	23·69
$C_2O_4H(NH_4) + \frac{1}{2}H_2O$	11°·5	5·80	6·26	15·97
$C_2O_4H(NH_4).C_2O_4H_2 + 2H_2O$	7°·75	2·46	2·52	39·68

On some Derivatives of Camphoric Acid. By F. WREDEN.†

Bromo-Camphoric Anhydride.—ON heating 1 mol. bromine with 1 mol. camphoric acid in presence of water to 170° and leaving the mixture to cool, long prismatic crystals, probably of the composition $C_{10}H_{16}O_4Br_2$, were obtained, which when exposed to the air are slowly resolved into bromine and camphoric acid. In the absence of water the reaction takes a different course, bromo-camphoric anhydride being formed:

$$C_{10}H_{16}O_4 + Br_2 = C_{10}H_{13}BrO_3 + HBr + H_2O.$$

To prepare this body, the author recommends that a mixture of 12 grm. camphoric anhydride and 18 grm. dry bromine be heated in a sealed tube for about three hours at 130°—140°. The contents of the tube are then washed out with ether, and the white powder so obtained is recrystallised from chloroform. It is less soluble in ether than camphoric anhydride; crystallises from strong boiling alcohol in small needles, but under partial decomposition. It dissolves undecomposed in 60 per cent. spirit at a temperature of 60°, and is readily soluble in chloroform, from which it may be obtained in transparent prismatic crystals.

* Zeitschr. f. Chem. [2], vii, 120. † Zeitschr. f. Chem. [2], vii, 97.

It blackens when heated to 100° and is not attacked by phosphorus pentachloride under the ordinary atmospheric pressure. This anhydride does not exhibit the usual behaviour with water characteristic of bodies of this class; on treatment with water or alcohol, the bromine becomes replaced by the OH or OC_2H_5 group. Higher brominated products were not obtained from camphoric anhydride.

Oxycamphoric Anhydride is prepared by heating bromocamphoric anhydride with water in a flask connected with an inverted condenser. If the bromo-anhydride contains camphoric anhydride, the product will contain camphoric acid also. To remove this, it is converted into the lead salt, whereupon insoluble plumbic camphorate is formed, which may be filtered off, and the oxy-acid then set free by sulphuric acid. Oxy-camphoric anhydride melts at 201°, and if heated for some time at 200° begins to decompose; it is soluble in ether and alcohol, also in water, but in this case it melts first; it also separates out as an oil on cooling from a hot saturated aqueous solution. It crystallises with one or two molecules of water, but becomes anhydrous on standing over sulphuric acid *in vacuo*.

Oxy-camphoric anhydride forms salts, all of which, with the exception of the sodium salt, are crystalline and soluble in water. The lead salt is difficultly soluble even in boiling water; the barium and silver salts decompose when heated with water; a volatile oil escapes and barium carbonate or silver remain. The cadmium salt, $Cd(C_{10}H_{13}O_4)_2 + 3aq.$, crystallises in transparent prisms which lose their water at 100°. The ether, $C_{10}H_{13}(C_2H_5)O_4$, forms prismatic needles, which melt at 63° and sublime below 100 , readily soluble in alcohol, ether, chloroform, and carbon bisulphide, slightly in boiling water which is without action on it. It is saponified by heating with potash solution.

By the action of PCl_5, oxy-camphoric anhydride is converted into the corresponding chloride, from which water regenerates $C_{10}H_{14}O_4$.

On heating the calcium salt of oxy-camphoric anhydride an oil is obtained, which, after heating with sodium in a sealed tube to 100°, boils at 118°—120° and has the composition C_8H_{14}. The vapour-density was determined as 3·75 (calculated 3·8) :—

$$C_{10}H_{14}O_4 = C_8H_{14} + 2CO_2.$$

The same body is formed by heating oxy-camphoric anhydride with water to 180°, carbonic anhydride and carbonic oxide being evolved; and probably also by heating the anhydride to 150° with hydriodic acid solution.

Camphoric Acid and Hydriodic Acid. On heating 4 grm. camphoric acid with 8 c.c. hydriodic acid solution (sp. gr. 1·7) to 200° for not longer than eight hours, the gases formed—carbonic oxide and carbonic

anhydride—being allowed to escape from time to time, a heavy oil of no constant boiling point and containing iodine is formed, from which the hydrocarbon C_8H_{14} was obtained after distillation over caustic lime and subsequent treatment with sodium. On further heating the oil containing iodine ($C_8H_{14}HI$?) for nine hours with hydriodic acid solution to 200°, the hydrocarbon C_8H_{16} was obtained.

H. E. A.

On the Nature and Constitution of Tannic Acid. By HUGO-SCHIFF.*

THERE is no doubt that crude tannic acid contains glucose, and that this substance is not merely mechanically retained in it; the percentage of sugar, however, has been very variously estimated by different observers, and it has been found possible, by appropriate treatment, to reduce its amount to within a few per cent., the tannic acid thus purified exhibiting precisely the same properties as before. It has, therefore, long been a matter of dispute whether tannic acid was to be considered as a glucoside or not. The following experiments of the author seem to throw important light on the subject.

A mixture of well-purified, crystallised tannic acid, dried at 110°, with phosphorus oxychloride of the consistence of an emulsion, was heated first at 100°, afterwards at 120°; much hydrochloric acid was evolved. The tannic acid thus finally converted into a yellow powder was first washed several times by decantation with dry ether, the residue freed from ether by gentle warming, and then dissolved in a small quantity of water. At the end of twelve hours a crystallisation of unchanged tannic acid (about 10 per cent.) was obtained. On saturating the yellow-red mother liquor with salt, the whole solidified; and on the addition of more salt, the precipitated mass caked together to a resinous mass, from which the greater part of the salt-solution could be poured off. After twice washing with salt-solution, the resinous cake was dried in vacuo, dissolved in absolute alcohol, and a considerable volume of ether was added to the solution, which was then filtered; after distilling off the ether, the mass was dried in vacuo. The varnish-like slightly-coloured residue exhibits all the reactions, solubility, physical properties, taste, &c., characteristic of tannic acid. It is the first tannic acid which has been prepared *perfectly free from sugar*. By heating with hydrochloric acid it was *entirely* converted into crystalline gallic acid and this again into tannic acid. Analyses of various portions gave 51·7 to 52·3 per cent. C. and 3·4 to 4·1 per cent. H. This proves tannic acid to be an alcoholic anhydride of gallic acid; in all probability it is a digallic acid. The following formulæ express the relation between the two acids:—

* Deut. Chem. Ges. Ber., iv, 231.

$$C_6H_2\left\{\begin{array}{l}COOH\\OH\\OH\\OH\end{array}\right.$$

Gallic acid.

$$C_6H_2\left\{\begin{array}{l}COOH\\OH\\OH\\O\end{array}\right.$$
$$C_6H_2\left\{\begin{array}{l}OH\\OH\\COOH\end{array}\right.$$

Tannic acid.

The compound present in the plants which yield tannic acid is probably a very unstable glucoside of a polygallic acid, perhaps of the composition indicated by Strecker. The least purified tannic acid is then the purest, since it contains the largest proportion of sugar.

H. E. A.

On the Formation and Decomposition of some Chlorinated Acids.

By J. G. Buchanan. No. I.*

When monochloracetic acid, or one of the isomeric monochlorpropionic acids, is heated with water, it gradually decomposes, the more quickly the larger the quantity of water and the higher the temperature. On the contrary when glycollic acid, or one of the isomeric lactic acids, is treated with hydrochloric acid, double decomposition takes place, and the corresponding chlorinated acid is formed.

This portion of the author's paper contains the results of his experiments on monochloracetic acid when heated with a large excess of water to 100°. Ten cubic centimetres of the solution employed contained ·324 grm. acid, corresponding to the formula $C_2H_3ClO_2 + 164H_2O$, and was found to be unaltered after the lapse of four months, from which it may be inferred that at the ordinary temperature the decomposition of an aqueous solution of monochloracetic acid takes place with extreme slowness. In each experiment 10 c.c. of the solution were enclosed in a sealed tube and then plunged into boiling water, and at the termination of the experiment cooled as quickly as possible. The extent of the decomposition was ascertained by determining the acidity of the solution by means of a standard solution of soda or baryta. I, represents the number of hours the solution was heated; II, the percentage of $C_2H_3ClO_2$ decomposed:—

I.	·0	2	4	6	11	14	16	18	21	24	27	30
II.	0·0	6·0	11·0	14·5	23·0	28·0	31·5	35·0	38·0	42·5	45·0	51·5
I.	33	37	43	48	72	96	120	144	192	332	430.	
II.	53·5	56·0	62·5	66·0	76·5	82·0	87·5	90·5	93·0	97·0	97·5.	

C. E. G.

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* Deut. Chem. Ges. Ber., iv, 340–342.

On the Quantivalence of Phosphorus and on the Action of Phosphorous Chloride and Bromine on Benzoic Acid. By A. GEUTHER and DR. A. MICHAELIS.*

THE authors consider that the researches of H. Wichelhaus (*Ann. Ch. Pharm., Supp.* vi, 257), do not prove the trivalent nature of phosphorus in its oxychloride.

By causing phosphorous chloride and bromine to act upon benzoic acid as described by Wichelhaus, they find that the reaction does not take place in the way he mentions, and that the substance obtained by him, boiling at 135—137°, which he supposed to be $PCl_2(OBr)$, is a mixture of phosphorus oxychloride and oxybromide. On repeating the experiment, acetic acid being substituted for benzoic, the authors found the reaction to be analogous, but that by a further action a substance, probably a chloride derived from bromacetic acid, is also produced.

Wöhler's benzoyl bromide (action of bromine on bitter almond oil) dissolves in warm phosphorus oxychloride; on distillation at 196—200° much carbon separates; neglecting the extreme action indicated by the separation of carbon, the change which occurs may be expressed by $3C_7H_5OBr + PCl_3O = 3C_7H_5OCl + PBr_3O$. Since, then, phosphorus oxychloride and benzoyl bromide cannot exist together, any bromine that may be contained in the final product of the action of PCl_3Br_2 on benzoic acid must exist, not as benzoyl bromide, but as phosphorus oxybromide.

F. H. H.

On Organic Derivatives of Sulphuric Acid. By HERMANN KAMMERER.†

CARIUS and Kämmerer, observing that the sulphobenzoic acid, which they obtained by the action of silver sulphate on benzoyl chloride, was, as they thought, decomposed on evaporation of its aqueous solution, with separation of sulphuric acid, held it, for this reason, to be different from the sulphobenzoic acid obtained from sulphuric anhydride and benzoic acid. Oppenheim, after a comparison of the acid barium salts of the two acids, lately came to the conclusion that the two are identical. The author now states that he had already come to the same conclusion, and that the erroneous statement that decomposition took place on evaporation is explained by the fact that the barium is not immediately and perfectly precipitated by dilute sulphuric acid from a solution of the acid barium salt.

* Zeitschr. f. Chem. [2], vii, 158, from Jenaische Zeitschr. vi, 242.

† Deut. Chem. Ges. Ber., iv, 219.

The author has further studied the action of silver sulphate on iodoform, chloracetic acid, and ethyl iodide, all of which seem to be decomposed without formation of by-products. The iodoform product gave a barium salt crystallising in characteristic microscopic scales, which exhibit the remarkable resistance to the action of oxidising agents peculiar to the salts of *methintrisulphonic* acid. In composition, however, it does not seem to be identical with the latter; the air-dried salt containing 46·8 per cent. of barium and 3·32 per cent. of water, whereas barium methintrisulphonate contains 15 per cent. water, and when anhydrous 44·7 per cent. of barium. From two different preparations salts were obtained, exhibiting apparently, under the microscope, different forms; it is, therefore, possible that two isomeric or two different acids are formed.

On heating 2 mols. chloracetic acid with 1 mol. silver sulphate and an adequate quantity of water for 24 hours, the whole of the silver disappears from solution. A barium salt was prepared from the product, but on evaporation on the water-bath, it underwent partial decomposition, with separation of barium carbonate; neither could lead, copper, or silver salts be obtained, as their solutions on standing were decomposed, with separation of metallic sulphide. It would seem, however, that pure barium and sodium salts can be prepared by precipitation with alcohol.

Monochlorobenzoic acid is not affected by heating with silver sulphate in sealed tubes.

Ethyl iodide is readily decomposed, and yields a product, with the investigation of which the author is at present engaged.

H. E. A.

On the Formation of a Methyl-isethionic Acid. By E. Erlenmeyer.*

From the formula of isethionic acid $\begin{array}{l} CH_2(OH) \\ CH_2.SO_2(OH) \end{array}$, it is evident that two isomeric acids could be produced by the substitution of methyl for hydrogen, according as the substitution took place in one or other of the two constituent carbon groups. One of these acids should be produced by the action of an acid sulphite of alkali-metal on propylene oxide, just as isethionic acid is formed from such a sulphite and ethylene oxide; experiment confirms this reasoning. By the action of SO_3, &c., on isopropylic alcohol (which should give rise to the acid $\begin{array}{l} CH(OH).CH_3 \\ CH_2.SO_2(OH) \end{array}$,

* Ann. Ch. Pharm., clviii, 260—262.

it is hoped that the structure of the methyl-isethionic acid thus got from propylene oxide may be made clear, according as the two acids are found to be identical or dissimilar.

C. R. A. W.

On Benzene-sulphonic Acid. By M. ASCHER and VICTOR MEYER.*

THE experiments detailed in this communication were undertaken with the object of determining the identity or non-identity of the benzene-sulphonic acid obtained by Schmitt,† by the action of absolute alcohol under pressure on the diazo-derivative of sulphanilic acid, with the acid from benzene and sulphuric acid. Schmitt believed he had observed certain differences in the properties of his acid, and, therefore, considered it to be isomeric, and not identical, with ordinary benzene sulphonic acid.

Were the existence of two such isomeric acids proved, it would be one of the very few facts at variance with Kekulé's benzene theory, which admits of the existence of only one *mono*-derivative; and it was, therefore, of extreme importance to obtain conclusive evidence on this point. With regard to the two isomeric pentachlorobenzenes of Jungfleisch and Otto, of which, according to Kekulé's hypothesis, *no* isomerides are possible, the authors advance the suggestion that the one may possibly contain several molecules condensed into one, or even be a mixture of 1 mol. tetra- with 1 mol. hexa-chlorobenzene crystallised together, since Fittig,‡ by nitration of a mixture of 1 : 3 with 1 : 4 xylene, obtained a pure trinitroxylene melting at 129·5°, which he ascertained to be a compound of trinitro 1 : 3 and trinitro 1 : 4 xylene, and also succeeded in obtaining artificially by crystallising a mixture of the two pure isomeric nitro-bodies; it seems, therefore, highly probable that the chlorobenzenes may exhibit similar phenomena.

The sulpho-acid was prepared exactly according to Schmitt's directions, and from it the potassium salt, which, after repeated recrystallisation from alcohol was directly compared with that of the ordinary acid and found to be identical with it in all respects. Again, no difference whatever could be detected between the chloride, $C_6H_5SO_2Cl$, and amide, $C_6H_5SO_2NH_2$, prepared from either acid. The amide from both sources melted exactly at 147°—148°. The anilide

$$C_6H_5SO_2N \begin{cases} H \\ C_6H_5, \end{cases}$$

obtained by the action of aniline on the chloride, was also identical with the known benzene-sulphanilide. Finally, the solubilities in water of the benzene-sulphamides from the two sources were deter-

* Ber. Deut. Chem. Ges., iv, 32. † Ann. Ch. Pharm., cxx, 152.
‡ Ann. Ch. Pharm., cliii, 276.

mined, and found to be identical; 1000 parts of water at 16°, dissolved 4·3 parts of each. In fact, all the observations made prove beyond doubt the identity of the two acids; the differences observed by Schmitt were no doubt due to the presence of impurities.

H. E. A.

On the Constitution of Chrysanisic Acid. By H. SALKOWSKI.*

THE author's experiments have led him to the conclusion that the constitution of chrysanisic acid, a product of the action of fuming nitric acid on nitranisic acid, is represented by the formula

$$C_6H_2(NH_2)(NO_2)_2COOH.$$

i.e., it is an *amidodinitrobenzoic acid.*

The following three reactions go to prove this:

1. On reduction with tin and hydrochloric acid, it yields an amido-derivative of the formula $C_7H_9N_3O_2$, of which the hydrochloride $C_7H_9N_3O_2.2HCl$, and stannoso chloride $C_7H_9N_3O_2.2HCl + 2SnCl_2$, were obtained.

2. By digestion with fuming hydrochloric acid at 200°, it is converted into a monobasic acid of the formula $C_7H_3Cl_3O_2$, *i.e.*, *trichlorobenzoic acid.* This reaction, originally undertaken with the view of ascertaining the possible presence of the methoxyl group, is interesting as the first instance of the replacement of the nitro-group by chlorine by the action of hydrochloric acid. It may be expressed by the following equation :—

$$3C_7H_5N_3O_6 + 11HCl = 2C_7H_3Cl_3O_2 + 5NH_4Cl + 2N_2 + 7CO_2,$$

and, in fact, ammonium chloride, nitrogen and carbonic anhydride were observed as products.†

The trichlorobenzoic acid thus obtained is isomeric with that of Jannasch (*Ann. Ch. Pharm.* cxlii, 301), prepared by oxidation of trichlorotoluene, and of Beilstein, (*Ann. Ch. Pharm.* clii, 234) prepared by the oxidation of trichlorotoluene trichloride, and by the action of chloride of lime on benzoic acid. It melts at 203° (Beilstein's at 163°). Its calcium and barium salts crystallise respectively with six and four molecules of water (Beilstein's with 2 and $3\frac{1}{2}$), which they do not lose over sulphuric acid. The ethyl-ether melts at 86° (Beilstein's at 65°).

3. From the mode of formation of chrysanisic acid, the presence of

* Ber. Deut. Chem. Ges., iv, 223.

† The author finds hydrochloric acid to be without action on nitrobenzoic acid; picric acid yields a chlorinated product, probably dinitrochlorophenol.

an amido-group was to a certain extent improbable; an attempt was, therefore, made to obtain a diazo-derivative from it, but unsuccessfully. On the other hand, it was readily converted into *dinitro-oxybenzoic* acid by the action of nitrous acid on its boiling aqueous solution, an almost theoretical yield being obtained. The acid thus formed crystallises from the aqueous solution in yellowish rhombic plates, often more than an inch long, and melts with decomposition at about 235°. The ether, prepared by the action of hydrochloric acid on an alcoholic solution of the acid, forms fine colourless needles, melting at 84°. The properties of the dinitroxybenzoic acid thus obtained differ from those of dinitrosalicylic acid, and of the dinitroparaoxybenzoic acid prepared by Barth.*

H. E. A.

On the action of Chlorine on Aldehyde. By G. KRAEMER and A. PINNER.†

IN this communication the authors describe at length their experiments on the action of chlorine on aldehyde, undertaken chiefly in the hope of thus obtaining chloral, and being able to utilise the valueless residue from the first runnings obtained in the distillation of crude spirit, which consist mainly of alcohol, aldehyde, and paraldehyde.

Chlorine was passed into aldehyde, at first carefully cooled in a freezing mixture, and only heated to 100° at the close of the reaction. The first few bubbles caused the separation of a small quantity of solid metaldehyde, whether originally present in the aldehyde or formed by the reaction is undecided. After a short time, evolution of hydrochloric acid set in and every trace of chlorine was absorbed. With 100 grms. of aldehyde, at the end of 24 hours, no further absorption took took place, even at 100°. The resulting brown mass consists of two layers: a lower, darker, almost solid, and an upper, lighter coloured liquid layer. The latter is a saturated solution of hydrochloric acid and the bodies of the lower layer in water. As it was found impossible to separate these two well, the whole was submitted to distillation. A considerable quantity passed over between 90° and 100°; the thermometer then rose rapidly to 160°; and the main product distilled over between this and 180°; the temperature again rose to about 240°, but only decomposition-products were obtained, and a considerable carbonaceous residue remained in the flask. The authors did not succeed in any case in detecting acetic acid, acetyl chloride, or the body $C_4H_7ClO_2$. The simplest

* Zeitchr. f. Chemie, 1866, 645. † Ann. Ch. Pharm., clviii, 37.

and quickest method of purifying the portion boiling at 160°—180° was found to be fractional distillation. By this means a body boiling at 163°—165° was isolated, which proved to be *crotonic chloral.*

Trichlorcrotonic aldehyde, $C_4H_3Cl_3O$. This is a colourless oil of peculiar odour, somewhat recalling that of ordinary chloral; it combines with water to a crystalline hydrate, the reaction being attended by a considerable rise of temperature; on mixing it with alcohol, much heat is evolved, but no crystalline compound is formed. It is readily decomposed by alkalies; fuming nitric acid converts it into the corresponding trichlorinated acid. In short, in chemical behaviour, it corresponds in every respect with the trichloraldehyde of the acetic series. A vapour-density determination gave 86·01(H=1), the theory requiring 86·75. Its formation is easily explained, since Kekulé has shown that aldehyde is readily converted into crotonic aldehyde by the action of dehydrating agents:

$$\left\{\begin{matrix} CH_3-COH \\ COH-CH_3 \end{matrix}\right. = CH_3-CH{=}CH-COH + H_2O.$$

Now gaseous hydrochloric acid is one of the most effective agents of condensation, and by the first action of chlorine on aldehyde, hydrochloric acid is formed; and this, reacting on the aldehyde, effects its conversion into crotonic aldehyde, which then becomes gradually chlorinated.

Crotonic Chloralhydrate, $CCl_3-CHCH-CH\left\{\begin{matrix} OH \\ OH \end{matrix}\right.$. This compound may be readily recrystallised from water, forming thin, dazzling white, shining plates, which pertinaciously retain water and melt at 78°. It is very volatile in a current of steam. It is difficultly soluble in cold, readily in hot water, very soluble in alcohol. Its vapour powerfully attacks the mucous membrane and the eyes.*

Dichloroallylene, $C_3H_2Cl_2$. The decomposition of ordinary chloral by alkalies into chloroform and formic acid rendered it probable that crotonic chloral would yield allylic chloroform and formic acid:

$$CCl_3-CH{=}CH-COH + KHO = CCl_3-CH{=}CH_2 + HCOOK.$$

In fact such a body does seem to be formed in the first instance; but it is immediately decomposed, with separation of hydrochloric acid:

$$CCl_3-CH{=}CH_2 = CCl_2{=}C{=}CH_2 + HCl.$$

Even the body thus formed is of no great stability; when perfectly dry it soon loses its pleasant odour, gives off hydrochloric acid, and smells of phosgene. It boils at 78°.

* On heating, crotonic chloralhydrate seems to split up into water, carbonic oxide, hydrochloric acid and dichlorallylene, a vapour-density determination giving 24·58 instead of 191·5. A decomposition into 8 vols. requires 23·9.

Dichlorodibromopropylene, $C_3H_2Cl_2Br_2$. This compound is formed from dichlorallylene, which readily takes up two atoms of bromine. It is a heavy, transparent, oily liquid of not unpleasant odour, which boils at 190° under partial decomposition. This body does not further combine with bromine; on heating it with two atoms of bromine to 100°, a colourless liquid is obtained and much hydrobromic acid is evolved, so that substitution, and not direct addition of bromine has taken place.

Trichlorocrotonic Acid, $C_4H_3Cl_3O_2$. A mixture of two parts of fuming nitric acid with one of crotonic chloral is allowed to stand for 12 hours, the vessel being surrounded by cold water. With pure chloral no immediate action takes place, but after some time a more or less violent evolution of red fumes. If immediate reaction take place, this proves the chloral to have been impure. The pure acid is obtained by distilling off the excess of nitric acid and collecting the portion boiling at 234° to 236°. (See Journal, p. 233.)

H. E. A.

Bromal, and the Bye-products of its Manufacture. By L. SCHAFFER.*

LOEWIG's method of preparing bromal was departed from, in so far as the bromine was added in the gaseous condition to the alcohol, and in relatively smaller quantity. The crude product of the reaction was distilled, first in a water-bath, and then on a sand-bath. What passed over below 100° consisted of ethyl-bromide and acetate (the latter in small quantity), hydrobromic acid, and some bromine. The portion which did not volatilise at 100° was separated by distillation into three fractions:—

(I.) Taken at 100°—130°, consisted principally of aqueous hydrobromic acid.

(II.) 165°—180°, bromal and an oily liquid, insoluble in water.

(III.) A small portion, boiling above 180°, with partial decomposition.

The bromal was separated from the second fraction, and pure bromal hydrate prepared from it by mixing with water and repeated crystallisation. Bromal and bromal hydrate having already been described by Loewig, it need only be mentioned that the former boils without decomposition at 172°—173°, and remains liquid at −20°. The hydrate melts at 53·5°; it breaks up on distillation, into water and bromal. Bromal forms with absolute alcohol, an alcoholate $C_2Br_3HO.C_2H_6O$, which crystallises in thick needles, melts at 44°, and is decomposed on distillation, in a manner analagous to the hydrate. That portion of the fraction of 165°—180°, which was insoluble in water, contained bromoform, and tetrabromide of carbon. The third fraction, boiling above

* Deut. Chem. Ges. Ber. iv, 366.

180°, when mixed with water, separated into two layers, one aqueous and acid, the other a heavy, oily liquid. This oily liquid solidified to a crystalline mass, on strong cooling; the crystals, when purified, showed the properties and composition of the tetrabromide of carbon described by Bolas and Groves. From the aqueous acid product from the third fraction, a barium salt was obtained, which proved to be barium dibromacetate. From the barium compound, dibromacetic acid and several of its salts were prepared. Dibromacetic acid is described as a white crystalline mass, which very readily attracts moisture to form a syrupy liquid. This eagerness for moisture interferes with the determination of the melting point of the acid; it appears to be between 45° and 50°. The acid boiled at 232°—234°, with slight decomposition.

Neither mono- nor tri-bromacetic acid was found among the products of the action of bromine on alcohol. Tribromactic acid is, however, readily obtained by oxidising bromal with fuming nitric acid. It appears in colourless tabular crystals, which melt at 130°, and boil at 245°, with production of bromine and hydrobromic acid. Several metallic tribromacetates are described, they are crystalline bodies, whose solutions are decomposed on a gentle heating, into metallic carbonate and bromoform. The free acid, in aqueous or alcoholic solution, breaks up in an analagous manner.

From the appearance of bromoform and tetrabromide of carbon among the products of the action of bromine on alcohol, Schäffer thinks it probable that tribromacetic acid is really formed, as well as dibromacetic acid; and that it is broken up by the heat of the reaction, and during the repeated distillations of the crude product.

W. H. D.

Researches on Valeraldehyde. By A. Schroeder.*

Pure valeraldehyde boils at 92·5°. By passing chlorine into it first in the cold and afterwards at a temperature of 145 as long as it is absorbed, the compound $C_{10}H_{12}Cl_6O$ is formed, according to the equation—

$$2C_5H_{10}O + 6Cl_2 = C_{10}H_{12}Cl_6O + H_2O + 6HCl.$$

This body may be considered as a substitution-product of the compound $C_{10}H_{18}O$, which was obtained by acting on valeraldehyde with lime (Fittig) or with zincethyl (Rieth and Beilstein) or by heating the aldehyde under pressure to 240° (Borodin). It is a liquid boiling at 203°—204°, and having a nauseous goaty smell; it does not combine with alkaline bisulphites, and is not acted upon by cold nitric acid; by boiling it with fuming nitric acid, a nitro-compound is formed.

* Deut. Chem. Ges. Ber., iv, 400.

On treating it with a boiling solution of caustic soda in alcohol, two molecules of hydrochloric acid are taken out, and the body $C_{10}H_{10}Cl_4O$ is obtained, which is an oily liquid having a pleasant smell of mint, and boiling at 208°—210°.

When valderaldehyde is imperfectly saturated with chlorine in the cold, *monochlorvalderaldehyde*, C_5H_9ClO, is formed, besides higher chorinated products.

The monochlorinated aldehyde is a liquid boiling at 134°—135°, and forming crystalline compounds with alkaline bisulphites.

Dry hydrogen sulphide does not act upon valeraldehyde; but when this gas is passed into its aqueous solution, white crystals separate, which, as proved by analysis and determination of vapour-density, consist of *sulphovaleraldehyde*, $C_5H_{10}S$. It is insoluble in water, soluble in alcohol and ether; from the hot ethereal solution it separates in asbestos-like crystals. Its smell is most offensive and persistent. It melts at 69°, and when heated very strongly, decomposes, giving off white fumes, having an indescribable smell; but it may be sublimed without decomposition *in vacuo*.

Selenovaleraldehyde is obtained by passing hydrogen selenide into the aqueous solution of valeraldehyde; it is a crystalline solid, which cannot be re-crystallised, as its solution in ether, alcohol, or methyl-alcohol soon decomposes, with separation of selenium in form of a mirror; but it may be purified, as it volatilizes in a current of gas with aqueous vapour at the common temperature. It forms white crystalline crusts, melting at 56·5°; its odour is exceedingly offensive, and produces difficulty of respiration and palpitation of the heart.

In contact with mercury it decomposes at 30°; it was therefore impossible to determine the vapour density. By acting on it with dry ammonia, *selenvaleraldine* is formed, a compound having the greatest resemblance to thiovaleraldine.

C. S.

New Compounds in the Camphor Group. By I. Kachler.*

By the action of nitric acid of specific gravity 1·37 on camphor in a retort there are produced, besides the previously known acids, camphoric, $C_{10}H_{16}O_4$, and camphretic, $C_{10}H_{14}O_7$, a volatile compound which floats on the top of the acid condensed in the receiver; this is more or less decomposed by washing with water or by distillation, and can therefore be purified from absorbed nitrous fumes, &c., only by passing through the liquid (separated from the acid distillate by a funnel) a stream of dry carbonic anhydride or air. The numbers obtained on analysis

* Deut. Chem. Ges. Ber., iv. 380.

agree with the formula $2(C_{10}H_{16}O)N_2O_5$. Water immediately decomposes this body, forming camphor and nitric acid. Caustic potash, however, does not produce this change, and hence the liquid may be partially dried by treatment with this reagent before passing the stream of dry gas through it.

The only analogous body yet known is the cinnamic aldehyde derivative $2(C_9H_8O).N_2O_5$ obtained by Dumas and Peligot.

From the mother liquors of the camphoric acid produced, a new acid crystallising in pearly scales can be obtained, the formula of which is $C_9H_{12}O_5$; and from this another acid $C_9H_{12}O_6$ can be obtained, resembling, in its deportment and the ease with which it crystallises, the commonest vegetable acids, *e.g.*, citric and tartaric.

C. R. A. W.

On a New Group of Colloïd Bodies containing Mercury, and certain Members of the series of Fatty Ketones. By J. EMERSON REYNOLDS.*

WHEN solution of mercuric chloride is slowly added to a mixture of acetone with dilute aqueous solution of potassium hydrate, the mercuric oxide first precipitated is dissolved, with production of a clear colourless liquid. This solution gelatinizes when heated to ebullition, or on the addition of acid in slight excess. On dialysing the alkaline solution, the diffusate, at the end of two days, contains a large quantity of potassium chloride, some potassium hydrate, and but a very small amount of mercury. If the process of diffusion be continued, the diffusate being replaced by pure water twice each day, until it no longer affords a cloud when treated with solution of silver nitrate, the dialyser will contain a pure colloïdal liquid, which, on careful evaporation to dryness, yields a resinoïd residue having a composition represented by the formula $\{(CH_3)_2CO\}_2Hg_3O_3$.

Water containing 2 per cent. of this compound retains its liquidity for months; a 5 per cent. solution remains liquid for some days, but produces a firm jelly on being heated to 50°. Adopting Graham's nomenclature, the liquid colloïd hydrate is the *hydrosol* of the new compound; and the gelatinous hydrate, the *hydrogel*. The *alcosol* may be obtained by adding to a 1 per cent. hydrate an equal volume of alcohol, and evaporating the mixture over quicklime until most of the water is removed. This *alcosol*, on being submitted to prolonged ebullition, yields a jelly or *alcogel* corresponding to that produced on heating the hydrate—in the former case alcohol, and in the latter water, being associated with the mercuric ketone compound. The compound must therefore be regarded as a strongly marked

* Proc. Roy. Soc., xix, 431—442.

member of Graham's group of these colloïds, though chemically differing widely from previously described compounds of this class.

Although the hydrate of this mercuric ketone-compound is neutral to test-paper, the author regards it as an acid of a very feeble character, and probably quadribasic. It is easily decomposed into mercuric oxide and acetone.

Several ketones of the fatty series are capable of uniting with mercuric oxide in presence of alkali, to form compounds analogous to that obtained with acetone. The higher ketones being insoluble in water, though soluble in alcohol, it is extremely difficult to prepare the colloïdal hydrates or hydrosols of the mercuric compound; but the general reactions of the several solutions leave no doubt that the compound contained in each belongs to the group of colloïd bodies and not to that of crystalloïds. J. B.

On a New Phenylene-Diamine. By PETER GRIESS.*

ON distilling the two isomerides of diamido-benzoic acid obtained by the author from uramido-benzoic acid,† they split up according to the equation:

$$C_7H_8N_2O_2 = C_6H_8N_2 + CO_2.$$

The base thus obtained is the same from both acids; it is readily soluble in hot water, from which it crystallises on cooling in white, often reddish, rectangular quadratic plates; it is also very soluble in alcohol and ether. Although identical in composition with the two known phenylene-diamines, it differs considerably from them in properties, the melting and boiling points of the three bodies being as follows:

	Mt.P.	B.P.
α Phenylene-diamine (Hofmann).....	63°	287°
β Phenylene-diamine (Hofmann).....	140°	267°
New Phenylene-diamine	99°	252°

The *sulphate* of this *phenylene-diamine* crystallises in shining scales, readily soluble in hot, difficulty soluble in cold water. Dried between bibulous paper it has the composition, $C_6H_4(NH_2)_2,H_2SO_4 + 1\frac{1}{2}$ aq., and loses its water of crystallisation a few degrees above 100°.

The *platinochloride* is obtained as a brown-red precipitate on the addition of platinic chloride to a hydrochloric acid solution of the base.

On the addition of a concentrated solution of ferric chloride to a hydrochloric acid solution of the diamine, ruby-red needles separate out after a short time, which are the hydrochloride of a new base; this may be obtained by the addition of ammonia to a boiling aqueous

* J. p. pr. Chem. [2], iii, 143. † Ber. Deut. Chem. Ges., ii, 436.

solution of the hydrochloride, in deep yellow microscopic needles, almost entirely insoluble in all neutral solvents. Their formula is probably $C_{12}H_{10}N_4$, and their formation is expressed by the equation:

$$2C_6H_8N_2 + O_3 = C_{12}H_{10}N_4 + 3H_2O.$$

H. E. A.

On Nitro-ortho-Toluidine. By F. BEILSTEIN and A. KUHLBERG.*

IN previous notices it had been shown by the authors that, on nitration of the acetyl-derivatives of para- and meta-toluidine, the nitro-group takes up the ortho-position; it was therefore interesting to ascertain what position it would assume in ortho-toluidine.

Nitro-ortho-acetotoluide, $C_7H_6(NO_2).NH(C_2H_3O)$, was obtained by adding ortho-acetotoluide to well-cooled nitric acid of 46·5 Baumé, and afterwards precipitating with snow. The precipitate, after repeated recrystallisation from alcohol, forms small yellow cubes. On slow evaporation, larger rhombic crystals were obtained, which melt at 101°—102°. It is readily soluble in alcohol, very difficultly even in boiling water. Decomposed by the necessary quantity of alcoholic potash-solution, it yields *nitro-ortho-toluidine*, which, when recrystallised from water, forms long, fine, saffron-yellow needles, melting at 133°—134°; readily soluble in acids, reprecipitated by ammonia. Its salts are of slight stability.

On converting this base into the sulphate of the diazo-compound, and decomposing this by absolute alcohol, a *nitrotoluene* was obtained, which distilled entirely at the temperature at which *meta-nitrotoluene* boils, and did not solidify at −20°. The toluidine prepared from this was liquid, like metatoluidine, but its acetyl-derivative did not exhibit a constant melting point.

The above facts are in perfect harmony with Hübner's observations on benzoic acid. Both para- and meta-chlorobenzoic acids gave nitro-acids, in which the nitro-group occupied the ortho-position; from ortho-bromobenzoic acid two nitro-acids were obtained, both of which held the nitro-group in the meta-position. Hübner's experiments render it probable that ortho-acetotoluide should yield two isomeric nitro-products, and this seems also to be the case.

H. E. A.

On some Derivatives of Meta-toluidine. By E. WRÓBLEVSKY.†

THE author separated para- and meta-toluidine by heating crude toluidine containing both forms, with rather more than the theoretical

* Zeitschr. f. Chem. [2], vii, 99. † Zeitschr. f. Chem. [2], vii, 135.

quantity of glacial acetic acid for 16 hours. On cooling, the greater part of the product solidified, but a considerable proportion of toluidine remained uncombined. On distilling it off, and again subjecting it to the same treatment, the product solidified after three days' rest, and consisted of pure *metatolylacetamide*. The crude product, as separated by distillation, fused at 98° (instead of 105°); but it had the same degree of solubility as meta-tolyl-acetamide, and its derivatives were wholly distinct from those of paratolylacetamide, and of great beauty and purity.

Bromotolylacetamide, $C_7H_6Br\ (NH.C_2H_3O)$. Metatolylacetamide suspended in water takes up bromine more readily than para-tolyl-acetamide, and but little resin is formed. It crystallises in brilliant long needles, melting at 156°—7°, easily soluble in alcohol and boiling water. The same compound is formed by the action of acetyl-chloride on bromotoluidine.

Bromotoluidine $C_7H_6Br.NH_2$, produced by decomposing the acetyl derivative with alcoholic potash distils over with steam and crystallises in large octohedrons, melting at 57°, and boiling with complete decomposition at 240°; easily soluble in alcohol, difficultly so in water.

The hydrochloride, $C_7H_6Br.NH.HCl$, crystallises from water in fine colourless, pearly, prismatic crystals, soluble in alcohol, volatile, and precipitated from its aqueous solution by concentrated hydrochloric acid. *The sulphate* $(C_7H_6BrNH_2)_2.H_2SO_4 + 1\frac{1}{2}H_2O$, crystallises from water in pearly white scales. *The nitrate*, $C_7H_6Br.NH_2.HNO_3$, crystallises from water in reddish-white needles, fusible with decomposition at 183°, 100 pts. water at 17° dissolve 4·92 pts. Treated with nitrous acid and alcohol it gave *ortho-bromo-toluene*, boiling at 182°, and oxidised by chromic acid to *ortho-bromo-benzoic* acid, melting at 153°.

o — m *dibromotoluene*, $C_7H_6BroBrm$, prepared by decomposing with absolute alcohol, the perbromide, $C_7H_6Br.N_2Br_2$, obtained from the above-mentioned bromotoluidine, is liquid at − 20°, and boils at 237°, its crystalline *nitro* derivative melts at 87·5°, from which *dibromotoluidine* crystallising in silky prisms, fusible at 83°, was prepared. These derivatives are identical with those obtained by the author from ortho-bromotoluene (Zeitschr. f. Chem. [2] vi, 239); from this it appears that in the bromination of *o*-bromotoluene the bromine takes up the *meta* position (*metastelle*). If the ortho-positions be represented by 1 : 2 and the meta positions by 1 : 3, an attraction of bromine atoms will be observed to take place, for dibromotoluene obtained directly differs from the *o*-brom-*p*-toluidine derivative (*loc. cit.*). The same action is now seen to occur with ortho-toluene. In the bromination of *p*-toluidine there exists a repulsion and in that of *m*-toluidine an attraction between NH_2 and Br.

Dibromo-m-toluidine, $C_7H_5Br_oBr_4(NH_2)_m$ is obtained by passing air

laden with bromine-vapour (4 atoms) into an aqueous solution of *m*-toluidine hydrochloride. The reaction is more active than with *p*-toludine. The product is distilled with lime and water. The free base crystallises in pearly needles easily soluble in alcohol, difficultly so in water, fusible at 50°. It does not combine with acids, and is isomeric with the three dibromotoluidines before described (ibid, v. 461; vi, 239).

o-Bromo-m-cresol, $C_7H_6Br_o(HO)_m$, is formed by treating o-bromo-m-toluidine with nitrous acid and crystallises in gold-coloured needles, sparingly soluble in alcohol and water, the aqueous solution being coloured greenish by ferric chloride; fusible at 88°·5 and decomposing on boiling.

F. H. H.

On Isomeric Tolylene-diamines.

By F. Beilstein and A. Kuhlberg.*

1. *Para-meta-tolylene-diamine*, $pmC_7H_6(NH_2)_2$. Obtained by reduction of dinitro-toluene, described by Hofmann (Jahresb. f. Ch. 1861, 512.)

Sulphate, $C_7H_6(NH_2)_2.H_2SO_4 + 2H_2O$.—Crystallises from water in long brilliant prismatic crystals which quickly turn red; is precipitated by alcohol from its aqueous solution, in crystals, 100 p. water at 19·5° dissolve 5·58° p. When treated with manganese peroxide and sulphuric acid, it does not give any substance resembling quinone.

2. *Para-ortho-tolylene diamine*, $p\text{-}oC_7H_6(NH_2)_2$.—Obtained by reduction with tin and hydrochloric acid of nitrated p-toluidine. By treating the product of the reaction with sulphydric acid, and distilling the evaporated filtrate with caustic lime, the free base is obtained in white flakes, boiling without any alteration at 265°, melting at 88·5°, tolerably soluble in cold, more soluble in boiling water. The aqueous solution of the base is unstable and presently becomes coloured. The *hydrochloride* crystallises in long needles, very soluble in water. *The sulphate*, $C_7H_6(NH_2)_2.H_2SO_4 + 1\frac{1}{2}H_2O$. Is precipitated by alcohol from its aqueous solution in pearly flakes. 100 p water at 19·5° dissolve 9·29 p. The free base and its salts oxidise in the air more quickly than p-m tolylene-diamine.

3. *Meta-ortho-tolylene-diamine*, $m\text{-}oC_7H_6(NH_2)_2$, obtained from nitrated meta-toluidine by the same method as the last-mentioned base, separates after reduction as a double salt of the composition $C\,H_6(NH_2)_2.2HCl.SuCl_2$, crystallising in pale yellow tables. This compound was decomposed by sulphydric acid, and the filtrate was

* Zeitsch. f. Chem. [2], vii, 134.

evaporated to dryness and distilled with quick lime. The free base is colourless and crystallisable, fusible about 80° and boils unaltered at 270°; it is even more unstable than p-o tolylene-diamine, rapidly becoming dark blue in the air, even though dry, which interferes with the determination of its melting point.

Sulphate $C_7H_6(NH_2)_2.H_2SO_4$.—Anhydrous, pulverulent, and sparingly soluble in cold water; it is more soluble in hot water but does not separate on cooling, unless alcohol be added. 100 p. water at 11·5 dissolve 0·84 p.

F. H. H.

On Thio-aniline and Thio-toluidine. By V. MERZ and W. WEITH.*

ON heating together a mixture of two molecules of aniline with one of sulphur, a continuous stream of hydrogen sulphide is evolved; the action requires some days heating in a retort furnished with a condenser inclined upwards, before the evolution of hydrogen sulphide ceases, and finally furnishes a thick oil consisting of unaltered aniline, an indifferent resin, and a new base. By distillation with water, the aniline is driven off; by boiling dilute hydrochloric acid, the base, along with some of the resin, is dissolved; and the base is freed from the resin either by evaporation to dryness, solution in water, and fractional precipitation with alkalies—or better, by partially precipitating the crude hydrochloride with alkali, filtering off and precipitating the filtrate separately, solution of the precipitate in mixed ether and alcohol, and precipitation of the sulphate from this solution by cautious addition of dilute sulphuric acid. By successive washings with etherized alcohol, and strong pressure, a white sulphate is thus obtained which is dissolved and precipitated by alkali, and for final purification redissolved in hydrochloric acid and reprecipitated by alkali. The numbers obtained by analysis agree well with those required for thio-aniline $\left.\begin{matrix}C_6H_4(NH_2)\\C_6H_4(NH_2)\end{matrix}\right\}S$.

By addition of litharge, this action between sulphur and aniline is much facilitated, the reaction being

$$2C_6H_5(NH_2) + S_2 + PbO = \{C_6H_4(NH_2)\}_2S + PbS + H_2O;$$

for this purpose the aniline (2 molecules) and sulphur (1 molecule) are heated to 150°—160°, and the litharge added little by little: much steam is evolved, and the mixture froths up considerably; when this ceases enough litharge has been added. The mass is heated for some time, and after cooling, exhausted with boiling alcohol; the substance left on distillation of the alcohol is treated as above described, and finally yields thio-aniline identical with that obtained by the former process.

* Deut. Chem. Ges. Ber., iv, 384.

Thio-aniline is scarcely soluble in cold, and but sparingly in hot water: readily in alcohol and ether and in benzol: from these solutions it crystallises in needles or plates, which melt below 100° under water, but at 105° when dry: on attempting to distil it, decomposition takes place, yielding aniline, hydrogen sulphide, and a coaly residuum. With oxidizing agents, *e.g.*, chlorine-water, potassium chromate, ferric chloride, &c., it yields characteristic colour-reactions. It forms two classes of salts; viz., mono-acid and bi-acid: thus, two hydrochlorides, $C_{12}H_{12}N_2S.HCl$ and $C_{12}H_{12}N_2S.2HCl$, have been prepared and analysed: also the platinum salt, sulphate, and oxalate, corresponding to the latter hydrochlorite. The salts have a strong acid reaction, the base itself reacting neutral.

During the purification by the process with sulphuric acid, the formation of an isomeric sulphate insoluble in water, and yielding a non-crystalline base was observed; this is reserved for further examination.

Thio-acetanilide $C_6H_4.NH(C_2H_3O)_2S$. This is obtained by the action of acetyl chloride on thio-aniline dissolved by benzol, or better by long continued distillation *per ascensum* of thio-aniline and glacial acetic acid. Melting point 213°—213·5°.

Thio-sulpho carbanilide. By heating thio-aniline and carbon bisulphide in alcoholic solution, hydrogen sulphide is evolved and a variable mixture of two compounds is produced, viz.:—

$$S\left\{\begin{matrix} C_6H_4.NH_2 \\ C_6H_4.NH \end{matrix}\right\} CS \quad \text{and} \quad S\left\{\begin{matrix} C_6H_4.NH \\ C_6H_4.NH \end{matrix}\right\} CS.^*$$

$$S\left\{\begin{matrix} C_6H_4.NH \\ C_6H_4.NH_2 \end{matrix}\right.$$

The resin obtained by the action of sulphur on aniline appears to be a product of the further action of sulphur on the thio-aniline first formed thus: $2.C_{12}H_{12}N_2S + S_2 = H_2S + C_{24}H_{22}N_4S_3$: the authors ascribe to it the constitution—

$$S\left\{\begin{matrix} C_6H_4.NH_2 \\ C_6H_3.NH_2 \end{matrix}\right.$$

$$S\left\{\begin{matrix} C_6H_3.NH_2 \\ C_6H_4.NH_2 \end{matrix}\right.$$

Thio-toluidine. Toluidine and sulphur react on one another just as aniline and sulphur, but still more readily: a resin containing sulphur is simultaneously produced. The thio-toluidine, purified in the same way as thio-aniline, resembles this base in most of its properties, and forms bi-acid salts having a strong acid reaction; the hydrochloride and

* The authors double this formula.—C. R. A. W.

sulphate, and the base itself were analysed, yielding numbers agreeing with those calculated.

Benzene vapour passed through boiling sulphur gives off hydrogen sulphide and forms a small quantity of an oil smelling like mercaptan. Phosphorus pentasulphide also yields hydrogen sulphide with benzene, and forms a sulphuretted body apparently containing phosphorus (phenylthiophosphate?) Red hot antimony sulphide is reduced by hydrogen, and similarly with benzene vapour forms hydrogen sulphide and a stinking oil containing diphenyl.

C. R. A. W.

Solvents for Indigotin. By V. WARTHA.*

A. A. DE AGUIAR and Alex. Bayer,† have described a method by which they obtained indigo in the pure state by solution and crystallisation from aniline. In addition to this, the author has found other solvents by means of which indigotin may be obtained in the crystalline state. Venice turpentine, at a temperature approaching its boiling point, dissolves indigo with the same blue colour as sulphuric acid or aniline, and on cooling, the indigotin separates in the crystalline state, and can be purified by washing with alcohol or ether. Boiling paraffin may also be employed, the solution having the fine red colour of indigo vapour; in fact, a dilute solution can scarcely be distinguished from an alcoholic solution of magenta. When cold the indigo crystals may be purified by washing with benzol. The paraffin solution transmits homogeneous red light and has the same spectrum as the vapour of indigo. Petroleum dissolves indigo with a carmine-red colour: spermaceti and stearic acid also dissolve it, the former with a violet, and the latter with a blue colour, it crystallises from Venice turpentine in fine blue tables, and from paraffin in prisms which closely resemble those of sublimed indigotin.

C. E. G.

On Phosphorus Bases. By E. DRECHSEL and FINKELSTEIN.‡

IN consequence of a publication of Hofmann's on "the direct substitution of alcohol-radicles for the hydrogen in phosphine," the authors make known some experiments of their own on this subject, which they conducted about five years ago, but have not since resumed.

On passing a current of dry phosphine into a solution of zinc-ethyl

* Deut. Chem. Ges. Ber., iv, 334, 335.

† Ann. Ch. Pharm., clvii, 366, p. 268 of this volume.

‡ Deut. Chem. Ges. Ber., iv, 352.

in absolute ether, which must be cooled by a mixture of ice and salt, the separation of a white pulverulent precipitate is observed, which gradually increases in quantity. The precipitate was collected on a filter, washed rapidly with absolute ether, and dried *in vacuo* over oil of vitriol. The body thus obtained continually exhales phosphine when exposed to the air, which renders its analysis a matter of difficulty; in one experiment, 31·64 per cent. phosphorus was obtained by oxidising it with nitric acid; ZnHP requires 31·88 per cent. P. The zinc phosphide is decomposed at once by cold water, with evolution of phosphine and formation of zinc hydrate. It is especially interesting for the ease with which it is attacked by chlorides and iodides; acetic chloride acts upon it energetically, but the product of the reaction has not been thoroughly examined. By heating together the zinc phosphide, ethyl iodide, and ether to 150°, ethyl-phosphine was produced; $1\frac{1}{2}$ hour's heating was sufficient to complete the reaction. There was thus obtained, besides zinc iodide, the double compound $2\left.\begin{matrix}(C_2H_5)_3\\H\end{matrix}\right\}PI + ZnI_2$, which was analysed with satisfactory results. Caustic potash, added to the aqueous solution of the double salt, sets free triethylphosphine, recognisable by its offensive smell.

The substitution of methyl or ethyl for hydrogen in phosphine, was also effected by saturating ethyl or methyl iodide with phosphine, and allowing the solution to stand for some time at the ordinary temperature, or by heating the solution to 100°. In this way, the monethyl—or mono-methyl phosphonium iodide $(CH_3)H_3PI$ alone is produced; more highly substituted phosphorus bases were not formed.

W. H. D.

On the Action of Phosphine on the Iodides of Methyl and Ethyl.

By A. W Hofmann.*

Not long since, Hofmann showed that substitution of an alcohol-radical for hydrogen in phosphine, could be effected by the action of alcohol on phosphonium iodide. In his experiment, he obtained hydriodide of triethylphosphine; it was hoped that mono- and diethylphosphine might also be produced in this reaction. The four following cases might be expected:—

$$4C_2H_5,HO + H_3P,HI = (C_2H_5)_4P,I + 4H_2O \quad (I)$$
$$3C_2H_5,HO + H_3P,HI = (C_2H_5)_3P,HI + 3H_2O \quad (II)$$
$$2C_2H_5,HO + H_2P,HI = (C_2H_5)_2HP,HI + 2H_2O \quad (III)$$
$$C_2H_5,HO + H_3P,HI = (C_2H_5)H_2P,HI + H_2O \quad (IV).$$

Numerous experiments were made, in which alcohol and phosphonium iodide, in the proportions expressed by equations III and IV, were

* Deut. Chem. Ges. Ber. iv, 372.

digested at different temperatures and for different periods of time: without, however, producing the primary or secondary phosphine. Following equation III, triethylphosphonium iodide, some phosphine, and a trace of tetrethylphosphonium iodide, are obtained. By working according to equation I, tetrethylphosphonium iodide, and triethylphosphonium iodide, are produced in nearly equal quantities. Digestion of the materials in the proportion expressed by II, gives rise to triethylphosphonium iodide in preponderating quantity, but considerable quantities of the tetrethylphosphonium iodide are also formed. In cases I and II, scarcely a trace of gas is produced. The recent communication of Drechsel and Finkelstein induced the author to extend and verify their observations. A solution of phosphine in dry methyl iodide was heated to 100° for five or six hours; there were thus produced, trimethylphosphine hydriodide and tetramethylphosphonium iodide. The same bodies are obtained by heating in sealed tubes, methyl iodide and phosphine, in presence of a saturated ethereal solution of zinc iodide.

Trimethylphosphine is noticed as a colourless, readily oxidisable liquid, which gave characteristic reactions with sulphur and carbon bisulphide.

Experiments were made with ethyl iodide and phosphine, alone, and in presence of ethereal zinc iodide. The action is not so quick as that induced by methyl iodide; in either of the two above-mentioned cases, triethyl- and tetrethyl-phosphonium iodides were produced. Hofmann considers that Drechsel and Finkelstein had tertiary and quaternary phosphonium salts under examination, and not a salt of the primary phosphine. This he confirms in a postscript, having obtained the primary methyl- and ethyl-phosphines, by a process not yet published. The hydriodides of these bases are decomposed by water, with brisk evolution of gas. The hydriodide produced by the action of phosphine on methyl or ethyl iodide, is expressly stated by Drechsel and Finkelstein to dissolve in water, without the least evolution of gas.

W. H. D.

Contribution to the History of the Sulphur-ureas. By A. Arzruni.*

On heating sulphate of amidobenzoic acid with a little water and an equivalent quantity of potassium sulphocyanate on a water-bath, a clear solution of sulphocyanate of amido-benzoic acid is obtained, a salt very readily soluble, and which may be separated from potassium sulphate by evaporating to dryness and exhausting the residue with alcohol. But if this solution is evaporated again, the residue no

* Deut. Chem. Ges. Ber., iv, 406.

longer dissolves in cold alcohol, the sulphocyanate having now been transformed into *monoxy-benzoyl-sulphur-urea* $\left.\begin{matrix}CS\\C_7H_5O_2\\H_3\end{matrix}\right\}N_2$ which crystallises from hot water or alcohol in small hard crystals. Its solution forms white precipitates with calcium and barium chloride, and with silver and lead nitrate. Ferric chloride produces a brown pecipitate without the slightest trace of a red coloration.

C. S.

Examination of a Himalaya Tea. By PH. ZÖLLER.*

THE author states that the difference in the quality of different samples of tea, arises not from their being the leaves of different species of tea plant, but partly from the nature of the soil and manner of cultivation, and chiefly from the age of the leaves, the youngest leaves, other things being the same, yielding the best tea. The constituents of the ash of leaves vary with their growth; the quantity of lime and silica increase, both absolutely and relatively with their age, whilst the potassa and phosphoric acid decrease; and, as the best tea is prepared from the youngest leaves, an analysis of the ash would appear to be the simplest method of determining the quality of a tea. In order to ascertain the truth of this inference, the author examined a specimen of very fine Himalaya tea, which had been placed at his disposal by Liebig. It was carefully made, of a fine black colour, and consisted of very young lancet-shaped leaves. It contained 4·95 per cent. water, and 5·63 of ash, 100 parts of which contained 39·22 of potash, 14·55 of phosphoric acid, and only 4·24 of lime. As the tea consisted of very young leaves, and its ash was so rich in potash and phosphoric acid, it was to be expected that it would yield a large amount of nitrogenous matter and of theine, and also of total extract. The nitrogen amounted to 5·38 per cent., and the extract obtained by infusing 100 grms. in three litres of boiling water twice successively, was 36·26 grms. In order to determine the theine, the tea was heated to 100° with slightly diluted sulphuric acid, treated with lead hydrate to remove the acid, and exhausted with 86 per cent. alcohol. The pale-coloured solution on standing deposited crystals, which appeared to be theobromine, and the mother-liquor from these was found to contain 4·94 per cent. theine. No theobromine could be detected in two samples of the best tea of commerce used for comparison. Peligot's analyses† are the only published ones giving such high numbers for nitrogen and theine.

* Ann. Ch. Pharm., clviii, 180—193. † Ann. Ch. Pharm., xlvii, 360.

The extract gave 3·56 per cent. nitrogen, and 4·04 of ash, the latter containing 55·15 per cent. of its weight of potash, 7·89 phosphoric acid, and only 0·95 lime. The exhausted leaves gave 2·26 per cent. nitrogen, and 1·80 of ash, containing only 7·34 of potash, but 25·41 phosphoric acid, and 10·76 of lime. It remains undetermined whether Himalaya tea is distinguished from Chinese tea by containing theobromine, but it would appear that the specimen examined was equal to the best Chinese tea. The numbers given above show how easy it is, by an analysis of the ash to detect a tea consisting of exhausted leaves which have been re-dried, since they became comparatively poor in potash-salts, and rich in lime. The author believes the value of tea as a beverage is due, not only to the theine it contains, but also to the other nitrogenous substances present, and to the large amount of potash salts.

C. E. G.

On the Saccharate of Sodium Chloride. By M. E. J. MAUMENÉ.*

MAUMENÉ has prepared a compound of cane-sugar and sodium chloride in larger and more distinct crystals than those obtained by Peligot. The crystals were sometimes a centimetre long, quite transparent and colourless, and had the form of orthorhombic prisms of about 136°. The chloride of sodium alone was estimated, and no formula is given for the crystals. The percentage of salt found (13·3) is the same as that in the compound described by C. H. Gill in this Journal (p. 271). The sugar contained in this body is possessed of its normal rotatory power for polarised light. Pure sugar was recovered from the crystals.

C. H. G.

Physiological Chemistry.

On some Properties of Egg Albumin. By A. PETIT.*

AFTER referring to a previous communication of his own, the author states that the albumin of eggs when heated with acids acquires new properties, and becomes precipitable by alkalies and ammonia like a metallic oxide. If, for instance, a clear solution containing one-tenth of white of egg in water be treated with potash or ammonia, it remains clear, unless the free alkali be neutralized, when slight clouding appears. If to 10 c.c. of this solution of albumin in water, 10 drops of concentrated acetic acid be added, it becomes precipitable by

* Compt. Rend., lxii, 503—506. † J. Pharm. [4], xiii, 14.

potash, but not by ammonia; but the acidulated liquid, when boiled, becomes precipitable both by potash and by ammonia. These modifications are accompanied by polarimetric changes, for the solution of albumin turns the ray 2 degrees to the right before, and 7 degrees after boiling with acetic acid. The addition of alkalies to the warm acetic solution, precipitates the whole of the albumin, even before the saturation point is reached. In a solution containing free acetic acid, the neutralization of one-sixth of the acid determines the complete precipitation of the albumin.

The same molecular changes and alteration in rotary powers are produced by alkalies. On adding 1 grm. of caustic potash to 75 c.c. of a one-tenth solution of white of egg, and saturating immediately with acetic acid, total precipitation of the albumin occurs without the application of heat.

Albumin from urine does not yield the same results.

The author thinks that the above phenomena are due to a dehydration produced by the more intimate combination of albumin with the acid or alkali, analogous to that which takes place when solutions of albumin are boiled.

Animal charcoal has the property of removing albumin from its solution in liquids, whether acid, neutral, or alkaline. This peculiarity may be serviceable in vegetable analysis.

Remarks on the preceding Communication. By M. Gautier.*

The albumin of the white of egg is composed of two distinct albumins, the one having its maximum point of coagulation at 63°, the other at about 74°. The ratio of these two albumins is 1 : 5. The first has a rotary power of 43° 2′, the second about 26′. Besides these, white of egg contains a caseous substance and lactoprotein.

Treated with water at 150°, it yields the following products which pass through a dialyser, besides insoluble matters. 1. A substance having the properties of casein. 2. A substance analogous to hypoxanthine. 3. An albuminoïd substance.

Egg albumin is an alkaline albuminate; its coagulation is preceded by the displacement of the base, and Wurtz's albumin is the acid of this albuminate.

T. S.

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* J. Pharm. [4], xiii, 16.

On the Constitution of Blood, and the Nutrition of Muscular Tissue. By William Marcet.*

Dr Marcet finds that blood is a colloïd fluid, but contains a small proportion of diffusible constituents, chlorides, &c. These seem necessary to preserve the blood in its fluid state. The amount of chlorine is remarkably constant. The alkalinity of blood chiefly depends on its crystalloïd constituents. Blood contains phosphoric anhydride and iron in a perfectly colloïd state; blood, as a whole, contains more phosphoric anhydride and potash than serum. This depends on the blood corpuscles which contain these substances to a large amount, and preserve them in an indiffusible state till their discoïd form is destroyed by the addition of water. A mixture of colloïd phosphoric anhydride and potash can be prepared artificially by dialysing a solution of potassium chloride and sodium phosphate. By dialysing these substances in certain proportions for a certain time, phosphoric acid, potash, chlorine, and soda are found in the colloïd fluid in similar proportions to those found in serum after 24 hours' dialysis.

Muscular tissue consists of three classes of substances:—

Class 1. The constituents of the muscular tissue in the complete stage of assimilation constituting the tissue proper, or that portion of flesh which is insoluble in the preparation of a watery extract. These consist of an albuminous principle and phosphoric anhydride with varying proportions of potash and magnesia.

Class 2. The material from the blood on its way to form Class 1. This consists of the same substances and in the same proportions relatively to the albumin as in Class 1, but in solution and in the colloïd state.

Class 3. The material from Class 1 in the effete state and on its way out of the muscle. This includes the same substances as the two others, but in a crystalloïd state along with a quantity of chlorine and soda. The phosphoric acid and potash are present in the exact proportion required to form a neutral tribasic phosphate or a pyrophosphate as the formula $2K_2O.P_2O_5$ can be equally $2K_2O.H_2O.P_2O_5$. The formation of $2K_2O.P_2O_5$ shows that the blood supplies muscle with a large proportion of potash, the only object of which is the removal of the phosphoric acid it contains.

Muscle contains in store a supply of nourishment equal to about one-third more than it requires for immediate use, so as to allow of muscular exercise during prolonged fasting.

The numbers representing the excess of phosphoric acid and potash in blood over the proportion of these substances in serum, bear to each other nearly the same relation as that which exists between the phos-

* Proc. Roy. Soc., xix, 465.

phoric acid and potash on their way out of muscular tissue, indicating that the blood corpuscles have the power of taking up and preparing the nutritive matter which they supply to muscle.

Although the proportions of phosphoric acid and potash contained in edible vegetables such as potatoes, flour, and rice vary much, yet the proportion of colloïd phosphoric acid and colloïd potash to the total quantity of these substances contained in those vegetables is nearly the same in them all, and the same as that in blood. This seems to show that these vegetables have the power of transforming the phosphoric acid and potash from the crystalline and diffusible into the colloïd or indiffusible state in tolerably definite proportions, and these substances are not fit to become normal constituents of blood or to nourish muscle till they have been transformed in this way.

There is a constant change or rotation in nature from crystalloïds to colloïds and from colloids to crystalloïds. The mineral substances which nourish plants are diffusible, plants transform them into colloïds, and animals re-transform them into crystalloïds and excrete them as such. Dead animal and vegetable tissues all return into crystalloïds decomposition.

T. L. B.

On the function of Cellulose and Lignin in the Structure and Development of Plants, and on their Comparative Nutritive Value. By M. PAYEN.*

BY prolonged action of dilute nitric acid M. Payen has succeeded in separating the various foreign substances which permeate and encrust the cellulose framework of certain vegetable tissues, and thereby effecting a chemical dissection of their cellulose skeleton. The framework so produced gives the characteristic reactions of pure cellulose.

With regard to the nutritive value of this substance the author quotes the results of the researches of Henneberg and Stohmann, which show that the ligneous tissue of fodder is composed of cellulose and encrusting matter which differ in chemical nature and digestibility. The encrusting matter or lignin contains more carbon than cellulose does, and more hydrogen than oxygen; while cellulose contains hydrogen and oxygen in the proportion to form water.

It is the lignin which is the indigestible part of fodder. Cellulose is not indigestible, but its digestibility is considerably influenced by the degree of density of the tissue. Like some other substances, its assimilation is favoured, and its nutritive value enhanced, by the addition of fatty matter to the food.

D. F.

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* Compt. rendus, lxii, 457.

On the Composition and Digestibility of the substance associated with Cellulose in the fibre of Meadow Hay (Meissner and Shepard's Cuticular Substance). By TH. DIETRICH and J. KÖNIG.*

(Preliminary Notice.)

ALTHOUGH it seems certain from the results of numerous experiments that it is the cellulose element of vegetable fibre which is digested and assimilated by cattle, yet the authors think further investigation necessary, inasmuch as Meissner and Shepard have stated that it is the non-cellulose which is the source of the hippuric acid in the urine of herbivora,—a conclusion they came to from experiments on rabbits. As long as these animals were fed on carrots, potatoes, &c., their urine was free from hippuric acid, but when the fibre of hay or clover was added, hippuric acid invariably appeared in the urine. As cellulose was present in both cases, the source of the hippuric acid appeared to be the substance associated with cellulose in the vegetable fibre. This non-cellulose can be separated from the cellulose by boiling the fibre in nitric acid, sp. gr. 1·2, which dissolves only the non-cellulose. They consider it to be of the nature of Mohl's cuticular substance, and apparently not much differing from cellulose in its amount of carbon. Meissner and Shepard likewise found, on analysing the fibre which had passed into the fæces, that a considerable portion of the non-cellulose had disappeared.

The results arrived at by Dietrich and König differ considerably from those of Meissner and Shepard. They conclude from numerous experiments on vegetable fibre, and various modes of treatment, such as boiling with nitric acid, caustic potash, &c., that the chief part of the non-cellulose element of vegetable fibre does not consist of Meissner's cuticular substance, but that, in the fibre of meadow hay, as well as the corresponding fibre of the fæces, there exists a substance, or a complex of substances, in which is found a carbon percentage of from 55—66, and from 7—9 per centage hydrogen. (Cellulose = 44·4 C., 6·2 H., and 49·4 O.)

The ordinary modes of separating the non-cellulose from the cellulose of vegetable fibre are not altogether trustworthy, as the cellulose itself is acted on to some extent. The authors calculate the amount of non-cellulose in hay at 12 per cent. The amount existing in the fæces they calculate at 33 per cent. They hope to find in hypochlorite and hypobromite of potassium a better means of separating the two substances.

As regards the comparative digestibility of cellulose and non-cellulose, their experiments go to prove that the non-cellulose is little or not at all digestible, the digested part being almost entirely cellulose.

D. F.

* Zeitschr. f. Chem., vii, 153.

On the Metamorphoses and Migrations of the Proximate Principles in Herbaceous Vegetables. By P. P. DEHERAIN.*

THE author of this memoir states that the proximate principles of vegetables migrate from the older to the more newly formed leaves, and that this migration is associated with a transformation of glucose into cane-sugar, whilst when the seed is formed, the cane-sugar is converted into starch and the albumin into gluten—both insoluble. In this way the conversion of soluble into insoluble principles, and the accumulation of substances in the seed is accounted for, and it is illustrated by the following experiment:—If a porous vessel containing distilled water be placed in another vessel containing a solution of cupric sulphate, the salt penetrates by diffusion into the inner vessel. If then a few drops of baryta-water be added to the inner vessel, the salt is precipitated, the equilibrium is disturbed, and a new portion of cupric sulphate diffuses into the inner vessel. The salt may be again precipitated by baryta water, and the operations repeated till eventually the whole of the cupric sulphate will have passed into the porous vessel and there have been precipitated.

T. S.

Agricultural Chemistry.

On the Nitrogen supplied to the Soil in Manure, and not recovered in the increase of Crop. By J. B. LAWES and J. H. GILBERT.†

THE authors give an historical summary of their inquiries on this subject. They pointed out twenty years ago, that much of the nitrogen supplied in manure is never recovered either in the immediate or in the subsequent crops. At first, in accordance with the conclusions of De Saussure, Daubeny, Draper, and Mulder, they considered that the loss might be partly due to evolution of nitrogen by the growing crop. Subsequent results, some of which they published in the Philosophical Transactions for 1861, convinced them that this evolution does not take place, and that the loss of nitrogen must arise either from drainage or from accumulation in the soil in a state unfit for assimilation. Analyses of the soil of their experimental wheat field, published in 1866, showed that it retained a portion of the nitrogen supplied in manure, but that a still larger quantity was unaccounted for. Earlier results, obtained at Rugby from sewage irrigation, and published in 1865, had shown that a considerable loss of nitrogen might occur by its passing away as nitric acid in the drainage water. The authors, therefore, gladly provided Dr. Voelcker with samples of the drainage-

* J. Pharm. [4], xiii, 16. † Chem. News, xxiii, 241.

water of their experimental wheat-field, and the results of his investigation have been already laid before the Chemical Society.*

R. W.

Observations relative to the Life of the Barley Plant. By J. FITTBOGEN.†

THE plants were reared in pots, and sand purified by ignition, digestion with sulphuric acid, and washing till every trace of acid was removed, was used as an indifferent soil-material. Into glass cylinders were put first a layer of quartz rock, then of unsized cotton, and lastly the purified sand. 18 barleycorns were sown in each pot, at a depth of 2·5 cm., having been previously sprouted between two layers of damp filter-paper. The manure for each pot, expressed in milligram-equivalents was:—

KH_2PO_4	KCl	$MgSO_4$	$Ca(NO_3)_2$	Fe_2O_3	SiO_2
2·0	1·0	1·6	16·0	5·0	10·0

Thirty pots were so arranged. Plants were cut twice before the ear appeared and three times afterwards. There were thus five periods. The plants were merely divided into two parts,—that above the surface of the earth, and that beneath it, except in the last two periods, when a separation was made betwixt the straw and the seed.

The aërial organs of 100 plants contained on an average:—

Grams.	1st period.	2nd period.	3rd period.	4th period.		5th period.	
				Grain.	Straw and chaff.	Grain	Straw and chaff.
Organic matter..	11·821	44·083	106·667	41·250	99·896	74·654	80·308
Ash	1·854	3·400	4·567	1·000	3·563	1·388	3·767
Dry substance ..	13·675	47·483	111·234	42·250	103·459	76·042	84·075
Potash	0·748	0·951	0·957	0·229	0·459	0·235	0·495
Soda	0·045	0·066	0·089	0·009	0·112	0·012	0·104
Lime	0·223	0·569	0·924	0·058	0·980	0·087	1·045
Magnesia	0·075	0·216	0·282	0·095	0·237	0·149	0·168
Ferric oxide	0·021	0·031	0·088	0·022	0·035	0.131	0·137 ?
Phosphoric acid.	0·216	0·454	0·601	0·384	0·295	0.566	0·159
Silica.....	0·329	0·875	0·392	0·242	0·242	0·308	1·625
Chlorine	0·202	0·249	0.218	0·028	0·148	0·001	0·102
Nitrogen	0·897	1·605	1·714	0·661	0.951	0·937	0·732

* Page 283 of this volume. † Versuchs-Stationen Organ. xiii, 81; and Chem. Centr., 1871, 293.

The roots of 100 plants contained :—

Grams.	1st period.	2nd period.	3rd period.	4th period.	5th period.
Organic matter	6·158	16·669	23·027	25·677	20·764
Ash	2·006	1·739	1·663	1·873	1·538
Dry substance	8·164	18·408	24·690	27·550	22·302
Potash	0·230	0·165	0·157	0·159	0·079
Soda	0·118	0·114	0·125	0·106	0·087
Lime	0·652	0·648	0·588	0·611	0·645
Magnesia	0·108	0·072	0·047	0·039	0·033
Ferric oxide	0·053	0·043	0·046	0·079	0·075
Phosphoric acid	0·197	0·161	0·128	0·097	0·077
Silicia	0·590	0·517	0·538	0·715	0·483
Chlorine	0·050	0·041	0·031	0·039	0·035
Nitrogen	0·237	0·438	0·490	0·642	0·583

From the data given the following table was readily constructed :—

	100 Plants contained			100 Plants contained at the period of maturation				Hence there was found at the time of harvest more (+) or less (−) than was supplied in	
	A In the manure.	B In 33·3 kils. of sand.	Total of A + B *	In the grain.	In the straw and chaff.	In the root.	Total.	A.	A + B.
Potash.....	1·778	0·048	1·826	0·235	0·495	0·079	0·809	−0·969	− 1·017
Soda	—	0·993	0·993	0·012	0·104	0·087	0·203	+0·203	− 0·790
Lime.....	3·733	1·740	5·473	0·087	1·045	0·645	1·777	−1·956	− 3·696
Magnesia.....	0·267	0·759	1·026	0·149	0·168	0·033	0·350	+0·083	− 0·675
Ferric oxide ...	3·333	10·226	13·559	0·031	0·137 ?	0·075	0·243 ?	−3·090 ?	−13·616 ?
Phosphoric acid	1·183	0·319	1·502	0·566	0·159	0·077	0·802	−0·381	− 0·700
Silica.....	2·500	1.165	3·665	0·308	1·625	0·483	2·416	−0·084	− 1·249
Chlorine	0·295	?	0·295	0·001	0·102	0·035	0·138	−0·157	− 0·157
Sulphuric acid .	0·533	0·086	0·619	?	?	?	?	?	?
Nitrogen.....	1·867	—	1·867	0·937	0·732	0·585	2·252	+0·385	+ 0·385

Deducting 0·108 grm. of nitrogen supplied in the seed from the above 0·385 grm. there remains 0·277 grm. nitrogen derived from the nitrogenous compounds in the air.

The daily increase in the amount of ash was in the 1st period 0·386, in the 2nd period 0·116, in the 3rd period 0·078, in the 4th period 0·026, in the 5th period 0·012; whilst that of nitrogen was in the 1st period 0·113, in the 2nd period 0·083, in the 3rd period 0·011, in the 4th period 0·006, and in the 5th period 0. Consequently the most active assimilation of mineral matters and of nitrogen occurs during the

* No account is here taken of the ash-constituent in the seed sown.

early stages of growth, comprehending, according to the experiments, the first third of the whole period of vegetation.

The author also determined the relative proportions of phosphoric acid and nitrogen in the grain, and finds that in the unripe state the proportions are 1 : 1·72, and in the ripe grain 1 : 1·66. As regards the migration of nutriment from the root upwards, and from the stalks and leaves into the seed, the following was established. A translation of potash from the root into the upper portion of the plant appears to occur during the 3rd period, and of phosphoric acid and magnesia during the whole period of vegetation. In the 5th period the nitrogen decreased in the root and increased in the aërial portion of the plant. The absolute amount of nitrogen was markedly less in the aërial part of the plant during the period when the seed was forming (4th period), and higher in the root, than during the preceding stage of development. A passage of potash from the upper part of the aërial portion of the plant into the grain was noted in the 4th period. When the grain ripened, magnesia, phosphoric acid and nitrogen were given up to the seed.

As regards the increase of mineral matters, it was established that this is greatest during the first period. Lime, phosphoric acid, and silica increased up to the time of maturity of the seed, magnesia and soda up to the time of formation of the grain. After the third period the potash underwent a decrease, and the chlorine after the second period; and this, at the time of the ripening of the grain, had gone on to such a degree that of the former only 72 per cent., and of the latter only 48 per cent. of the maximum amount remained. The magnesia slightly decreased after the fourth period.

T. S.

Analytical Chemistry.

Analytical Notices. By Schönn.*

1. *Detection of Cobalt by means of Sodium Sulphocyanate.*—On adding one drop of a concentrated solution of cobalt to strong solution of sodium sulphocyanate, a blue coloration is produced, owing to the formation of a compound which crystallises either at once or after spontaneous evaporation, in long blue needles insoluble in carbon disulphide. When the cobalt solution is dilute, the colour appears only on warming. It is advisable to evaporate the cobalt solution nearly to dryness, add the sulphocyanate, and warm. In this way cobalt may be detected in one

* Zeitschr. f. Chem. [2], vii, 96, from Zeitschr. Anal. Chem., 1870, 209.

drop of a solution containing 0·0005 grm. in 1 c.c. Iron, nickel, zinc, and manganese do not interfere with the reaction, provided the solutions are neutral.

2. *Tincture of Guaiacum as Reagent.*—In the use of tincture of guaiacum for the detection of hydrocyanic acid, chromic acid, and ozone, great care is necessary. Guaiacum-paper moistened with solution of cupric sulphate is turned blue by ammonia, as well as by hydrocyanic acid. Tincture of guaiacum, in presence of sulphuric acid, is rendered blue, not only by chromic acid, but also by ferric chloride, potassium ferricyanide, gold chloride, potassium permanganate, molybdic acid, potassium nitrate and nitrite. Guaiacum resin assumes a blue colour with oxidising substances, and also with potassium antimonate, barium carbonate and hydrochloric acid, lead acetate, calcium chloride, manganese chloride, copper nitroprusside, mercurous nitrate, and sodium sulphocyanate. Copper salts also colour tincture of guaiacum blue when very dilute. The reaction is more sensitive in presence of ammonium chloride, barium chloride, ammonium bromide, potassium iodide or cyanide, or ammonium fluoride.

3. *Detection of Nitric Acid by Means of Brucine.*—The author calls attention to the fact that a solution of brucine in strong sulphuric acid is coloured rose-red, and subsequently yellow, not only by nitric and nitrous acids, but also by chlorine-water, hydrogen peroxide, potassium chlorate, chromic acid, potassium chromate, sodium hypochlorite, potassium ferricyanide and platinic chloride. Cupric chloride, gold chloride, and ferric chloride produce the same effect under certain circumstances.

4. *Behaviour of Potassium Iodide in presence of Cupric Sulphate.*—A mixture of potassium iodide and starch with so small a quantity of cupric sulphate that no iodine is deposited, was employed by Schönbein to detect hydrocyanic acid and metallic cyanides, with which it immediately produces a blue coloration. The author has observed that strong solutions of sodium, potassium, and ammonium chlorides and ammonium bromide, likewise set free iodine. Ammonium and potassium fluorides do not produce the blue coloration, and when present in quantity, even prevent the action of the cyanides, bromides, and chlorides. Hydrogen peroxide also produces an immediate blue coloration.

J. R.

On the employment of Bromine instead of Chlorine for Analytical purposes.

By Hermann Kammerer.*

The author finds that in all those cases where chlorine-water is generally employed, bromine-water, which is prepared with much greater

* Ber. Deut. Chem. Ges., iv, 218.

ease and expedition, can be equally well used, and often with advantage. Its action, in every instance where it depends on the formation of a hypobromite, is much more energetic than that of chlorine. For example, manganese, under the same conditions under which it is precipitated by chlorine on heating, is entirely thrown down by bromine in the cold, and even partly oxidised to permanganic acid. To ensure perfect precipitation of manganese in this way, it is, therefore, always necessary, after addition of an excess of bromine, to warm with a little alcohol. The detection of nickel in presence of cobalt in potassium cyanide solution by Liebig's method, often fails with an old chlorine solution; bromine-water, on the contrary, always retains its efficacy.

H. E. A.

On the Estimation of Carbonic Acid in Well Water. By K. KNAPP.*

THE author shows that the well known method of Pettenkofer for the estimation of carbonic acid in atmospheric air and in water is not always applicable, as supposed by Mohr, to spring waters, inasmuch as, when these waters contain lime, the *amorphous* carbonate (which has an alkaline reaction to turmeric, and is capable of neutralizing very dilute oxalic acid) appears to be formed. In order to obviate this difficulty, it is essential to boil the water after the addition of baryta water, &c. The author quotes the case of a water which when the boiling was omitted, appeared to contain absolutely no carbonic acid, but after the boiling gave 0·129 grms. of carbonic acid to the litre.

E. T. C.

Methods of Water Analysis by means of the "Hydrotimeter." By ALEXANDER MÜLLER.†

THE author describes certain methods of estimating sulphuric acid and chlorine in drinking waters, &c.. E. T. C.

On the quantitative Estimation of Hydrogen Sulphide in presence of Carbon Dioxide. By R. FRESENIUS.‡

THE methods described for the quantitative estimation of mixtures of hydrogen sulphide and carbon dioxide, do not allow of a direct weighing to be made of the gases. Moreover, they are complicated and not very accurate. With the view of finding a more exact and

* Ann. Ch. Pharm., clviii, 112. † Dingl Polyt. Jour., cxcix, 388.
‡ Zeitschr. anal. Chem., x, 75.

speedy method, the author instituted some experiments upon the power of hydrogen sulphide to decompose copper sulphate in different states of hydration, and found that that salt with one atom of water could be practically used for the retention of hydrogen sulphide. 14 grms. of pumice impregnated with copper sulphate, prepared by pouring 30 to 35 grms. of a hot saturated solution of copper sulphate over 60 grms. of pumice in pieces the size of a pea, and subsequently drying at 150°—160°, absorbed about 0·2 grm. of hydrogen sulphide. The method based upon this property of copper sulphate was tested, and found to give good results. In mixtures of the gases, soda-lime tubes were used in conjunction with the tubes containing the impregnated pumice. The apparatus is minutely described, and the precautions to be taken are fully given.

A. T.

On the Estimation of Phosphoric Acid. By CHARLES E. MUNROE.*

THE following is an outline of two processes devised by the author, out of a considerable number of experiments, undertaken with the view of improving upon the methods at present in use.

I. To the boiling phosphate solution, a weighed quantity of pure aluminium sulphate, previously dissolved, was added. A solution of mercuric chloride was then added, and finally pure sodium hydrate, until a precipitate of mercuric oxide was obtained which remained undissolved. In order to hasten the operation, the precipitate was allowed to settle, and the supernatant liquid poured upon the filter. The gelatinous precipitate was then evaporated to complete dryness in the manner recommended by Chatard, filtered by the aid of the Bunsen pump, ignited and weighed. The increase of weight over that of the alumina used was phosphoric oxide. It was found extremely difficult to burn the filter.

Test analyses performed upon anhydrous disodic phosphate, and crystallised ammonio-sodic phosphate, are quoted. The percentages of P_2O_5 obtained, scarcely differ from one another in the first place of decimals. Nevertheless, according to the author, the method applies with advantage only to the alkaline phosphates.

II. The second process described, is a modification of Rose's well known mercury process. The experiments were executed in the following manner. To a boiling solution of the phosphate, mercurous nitrate was added in slight excess. This threw down a lemon-yellow crystalline precipitate of nitro-mercurous phosphate. Mercuric nitrate was then added, and finally sodium hydrate, until a slight precipitate

* Sill. Am. Journ. [3], i, 329.

of mercuric oxide was obtained, which remained undissolved. The mixture of the two salts was found to be insoluble in both hot and cold water, and to wash like sand. The next step was to find a means of treating the nitro-mercurous phosphate, which should be readier than the fusion with alkaline carbonate, and subsequent estimation of the P_2O_5 in the form of pyrophosphate of magnesium, as recommended by Rose. Of the methods tried, the best was to mix thoroughly with a weighed quantity of cupric oxide, in a platinum crucible, with the filter placed on the top. The whole was ignited, at first gently, then to low redness at the mouth of a muffle, whereby the filter was in a few minutes completely consumed. After cooling, a few drops of nitric acid were added to oxidise the reduced copper, and again ignited until the weight became constant. The increase of weight was the phosphoric oxide, P_2O_5. After ignition the cupric oxide and phosphate came out of the crucible, in a beautiful coherent mass, leaving it perfectly clean and unharmed.

In this case also, the test analyses yielded highly satisfactory numbers, except in one or two instances, in which the mercury phosphate was imperfectly mixed with the oxide of copper. The process succeeded well with all phosphates, except those of iron and uranium. An attempt was made to replace the cupric oxide by stannic oxide, but with unsatisfactory results. The solution of mercurous nitrate employed in these experiments, was prepared by dissolving pure mercury in nitric acid, boiling till every trace of nitrous acid was driven off, and then permitting the solution to crystallise. A solution was made of these crystals and metallic mercury added to prevent the formation of mercuric nitrate.

In an Appendix the author gives some results, respecting the determination of arsenic and antimony, by precipitating these metals as sulphides, and collecting and washing the precipitates upon small cones of light porous earthenware, used in the place of paper filters. These cones bear a high temperature without change, and can even be substituted in some cases for crucibles.

J. W.

On the Estimation of Phosphoric Acid in Superphosphates.
By R. Warington.*

If the superphosphate contains soluble compounds of aluminium, it will yield less soluble phosphate when boiled with water than when exhaustion is conducted in the cold; this is shown by the fact that

* Chem. News, xxiii, 205.

alum added to a cold solution of superphosphate produces no change, but on applying heat aluminium phosphate is precipitated. Ferric salts act differently; they give an immediate precipitate in the cold. Most superphosphates contain traces of soluble aluminium salts; those prepared from aluminous phosphates may contain a considerable quantity; the amount, however, depends much on the manner of manufacture. The solutions in cold water of such superphosphates become turbid on boiling.

It appears from the above that the soluble phosphate should always be extracted with cold water. The residue then yields a further trifling amount of phosphoric acid on boiling, arising probably from decomposition of reduced phosphates. The author believes that the best method of extracting soluble phosphate is to take 10 grams of the superphosphate and elutriate them in a mortar with 1 litre of cold water. The water and suspended matter are poured into a bottle and shaken at frequent intervals during three hours. 100 c.c. of the solution correspond to 1 gram of the superphosphate.

The soluble phosphate is usually estimated by precipitation with ammonia, with or without calcium chloride according to the proportion of lime in the solution. This method is liable to several errors; analysts employing it should check their mode of work by some other method.

The soluble phosphate may be accurately estimated by uranium acetate if alumina be absent, or if alumina has been previously removed as phosphate by ammonium acetate.

A method available under all circumstances is to precipitate the solution of superphosphate with excess of ammonium oxalate, and treat the filtered liquor containing the alumina and phosphoric acid, with citric acid, ammonia, and magnesia mixture, determining the phosphoric acid as magnesium pyrophosphate.

The insoluble phosphates in superphosphate are generally estimated much above the truth. It is best to determine the *total* phosphate by one operation, and then by deducting the soluble phosphate to find the insoluble. The total phosphate may be determined by solution in hydrochloric acid, and precipitation from a cold dilute solution with a small excess of ammonia, just sufficient to turn turmeric red. If, however, the superphosphate contains iron or aluminium, the hydrochloric solution should be neutralised as far as possible without occasioning a precipitate, and then treated with excess of ammonium oxalate, and subsequently with citric acid and magnesia mixture as already described.

R. W.

On the causes of High and Low Estimations of Soluble Phosphates. By Dr. A. E. DAVIES.*

THE author describes the plan of analysis usually followed. The superphosphate is rubbed in a mortar with cold water, the solution decanted on to a filter, and the residue treated as before with cold water two or three times. The undissolved portion is then boiled with water several times, the solutions filtered, and added to the cold extract. The mixed solution is then precipitated with ammonia, calcium chloride being added if there is not sufficient lime to throw down all the phosphoric acid. When an excess of lime is present, the precipitate carries down lime mechanically which cannot be washed out. The "low analysts" always redissolve the precipitate in hydrochloric acid, and reprecipitate with ammonia, to remove excess of lime. The "high analysts" always employ excess of calcium chloride and do not redissolve the precipitate. The method adopted by the author is to redissolve the precipitated calcium phosphate in acetic acid, separate the lime as oxalate, and then precipitate the phosphoric acid with magnesia.

R. W.

Method of Working up Uranium Residues. By W. JANI.†

THE precipitate of uranic phosphate, &c., is strained off and dissolved without previous washing, in not too dilute sulphuric acid, and warmed with a little nitric acid to oxidise any reduced uranic oxide. The solution diluted with spring-water is boiled with commercial caustic soda till the sulphur-yellow of uranic phosphate has given place to the orange-yellow of sodio-uranic oxide, and ammonia ceases to be evolved. The precipitate is then washed by decantation, suspended in excess of solution of commercial sodium carbonate, and saturated with carbonic acid gas. If enough soda is present, the precipitate rapidly dissolves, leaving paper-fibre, &c., unacted on. The solution is warmed to decompose any acid calcium carbonate, filtered, and boiled down to dryness in platinum or clean iron vessels, and strongly heated to drive off half the carbonic acid. The heated mass is powdered and exhausted with water, whereby pure uranic oxide is obtained.

C. H. G.

On the more important Methods for Estimating Arsenic gravimetrically. By R. E. O. PULLER.‡

THE methods most frequently employed for the estimation of arsenic,

* Fres. Zeitsch. f. analyt. Chemie., p. 41—75.

† Chem. News, xxiii. 220. ‡ Chem. Centr., 1871, 219.

viz., as trisulphide, as ammonio-magnesic arsenate, respectively as pyro-arsenate, and as uranic arsenate, were subjected by the author to a most exhaustive examination, and the investigation conducted—as is clearly evidenced by the numerous and accurate determinations—with the greatest care and circumspection. We regret that space does not allow us to transcribe the paper more fully.

I. *Arsenious Sulphide.*—The author endeavoured to elucidate:—(1) to what extent As_2S_3 is soluble in water; (2) whether it can be dried completely at 100°, and whether a higher temperature is permissible; (3) whether it is necessary to add acid, and if so, how much, and whether excess of acid accelerates the precipitation, or not; (4) whether the sulphur with which the precipitate is mostly contaminated can be entirely dissolved out by carbonic sulphide, and what method of extraction recommends itself most; (5) whether the precipitate obtained by sulphuretted hydrogen from solutions containing arsenic acid is composed of the pentasulphide (As_2S_5) or of arsenious sulphide and sulphur, and whether the sulphur can in that case be removed with equal facility by means of carbonic sulphide.

A solution of known strength was carefully prepared by dissolving 4 grams of pure and dry arsenious acid in potassium hydrate, and the slightly acidulated (HCl) solution made up to a litre.

50 c.c. of this solution = ·200 grm. of As_2O_3 were mixed with 25 c.c. of hydrochloric acid (sp. gr. 1·112 to 1·12) diluted to 50 c.c., and a current of sulphuretted hydrogen passed through for an hour and a half, whereby the precipitation was completed.

The precipitate was collected on a weighed filter and carefully dried (since arsenious sulphide is even more hygroscopic than the paper itself) and weighed at intervals of several hours, till the weight remained perfectly constant. It amounted to ·2528 grm. It was next freed from adhering sulphur by washing with carbonic sulphide which had been well shaken up with mercury before rectification, and which left no residue on evaporation, and the filter once more dried. It now weighed ·2479 grm. The quantity of sulphur was checked by evaporating the carbonic sulphide. It amounted to ·005 grm.

A second experiment gave ·2510 grm. of a precipitate, and yielded ·0032 grm. of sulphur, leaving ·2477 of As_2S_3. The theoretical quantity should have been 0·24898. The arsenious sulphide was next tested for its purity by dissolving in ammonium carbonate, as well as sodium carbonate. It dissolved without leaving any residue, and was completely volatilized. After drying at 100°, the precipitate was heated for twenty minutes in a current of carbonic anhydride to 120° without suffering any loss; even at 150° to 160° no loss was perceptible. The precipitate produced by allowing the filtrate to stand for several days was pure sulphur, insoluble in ammonia, readily and

entirely soluble in carbonic sulphide. Sulphuretted hydrogen produced no further precipitate, even on heating.

50 c.c. of the arsenious solution were mixed with 25 c.c. of hydrochloric acid, and diluted to 500 c.c. A current of sulphuretted hydrogen was passed for one hour and a half, then a current of carbonic anhydride in order to remove the excess of sulphuretted hydrogen as much as possible. The precipitates obtained in two experiments amounted to ·2484 and ·2491 grm. of As_2S_3 and S. The amount of sulphur removed by carbonic sulphide amounted to ·0002 and .0001 grm., whilst the precipitates weighed now ·2483 and ·2492, instead of ·24848—the theoretical quantity required—showing that the solubility of arsenious sulphide is all but imperceptible, and that the extraction with carbonic sulphide may practically be neglected when the sulphuretted hydrogen is removed by a current of carbonic anhydride.

On adding 10 c.c. of hydrochloric acid, instead of 25 c.c. as before, the precipitation was still complete; but on passing sulphuretted hydrogen through the slightly acidulated solution, as prepared, without the addition of any more acid, only a slight precipitation took place, after passing the gas for 5 hours.

On the addition of 5 c.c. of acid to the solution, the arsenious sulphide was precipitated slowly, and the precipitation was completed after 3 to 4 hours.

30, 40, and 50 c.c. of acid added to 50 c.c. of the arsenious solution, instead of 25 c.c. only, did not accelerate the precipitation materially. The author concludes, therefore, that the solution should be made strongly acid, previous to the passing of the sulphuretted hydrogen.

In order to ascertain whether the arsenious sulphide can be completely freed from larger quantities of precipitated sulphur, 50 c.c. of the arsenious acid solution were mixed with 10 c.c. of a solution of ferric chloride (= ·740 of Fe_2O_3), and sulphuretted hydrogen gas passed for two hours. The precipitate of arsenious sulphide and sulphur was dried and weighed, and then extracted with carbonic sulphide, whereby in two experiments ·2481 and ·2480 grm. of As_2S_3 were obtained. The sulphur precipitated by sulphuretted hydrogen from a hot acidulated solution of arsenic acid (obtained by passing chlorine through an alkaline solution of arsenious acid and acidulating) was not equally amenable to carbonic sulphide. The author found H. Rose's observation confirmed, viz., that sulphuretted hydrogen reduces arsenic acid first to arsenious acid, before it precipitates the arsenic as trisulphide. He observed that the sulphur precipitated from a hot solution (75°) is so intimately mixed up with the arsenious sulphide, that it forms with the latter little globules from which ammonia does not extract the whole of the sulphur, and which equally resist extraction in the cold

by means of carbonic sulphide. The sulphur was, however, readily dissolved out by removing the precipitate, as much as possible, from the filter and digesting it with carbonic sulphide on a water-bath. He obtained in this manner ·2474 and ·2481 grm. of pure As_2S_3.

By passing sulphuretted hydrogen through a cold solution of arsenic acid the precipitation was not complete till the stream of gas had been continued for three days, and both arsenious sulphide and sulphur were obtained in a finely divided state, which augured well for the extraction with carbonic sulphide. It may be observed that the sulphur thus precipitated at the ordinary temperature corresponded closely with the theoretical quantities required, according to the formula, $As_2O_5 + 5SH_2 = 5OH_2 + As_2S_3 + S_2$. With the view of simplifying the troublesome operation of extracting the sulphur with carbonic sulphide, the precipitate was dissolved in aqueous ammonia, filtered and reprecipitated with hydrochloric acid, and it was found that, although sulphur is insoluble in pure ammonia, it is soluble to a slight extent in ammonic sulpharsenite, and assists in the formation of the sulpho-salt.

The author obtained good results by determining the arsenic indirectly in the precipitate produced by sulphuretted hydrogen—after drying till constant and weighing—by oxidation of the sulphur and precipitation as barium sulphate. Oxidation with potassium chlorate and hydrochloric acid generally involves a loss from the volatilization of the arsenic as arsenious chloride. Red fuming nitric acid, however, answers very well, because it boils below the melting point of the sulphur. The operation may also be effected after exhausting the sulphide on the filter with ammonia, then filtering and evaporating to dryness.

The method of oxidation in an alkaline solution (KHO), by passing a moderate current of chlorine through a warm solution containing excess of pure alkali, as well as the two other methods, usually give a little more sulphur on account of the precipitated barium sulphate retaining, as Fresenius has shown, a little potassium chlorate, chloride, or nitrate, especially the latter, which must be removed by fusion of the barium sulphate with sodium carbonate, dissolving the residue in hydrochloric acid, and precipitating again as barium sulphate. It is obvious that the indirect method of estimating the arsenic by determining the sulphur in the precipitate may likewise be controlled by direct estimation as ammonio-magnesic arsenate.

II. *Ammonio-magnesic arsenate*, $MgNH_4AsO_4 + 6OH_2$. Obtained by drying *in vacuo* over concentrated sulphuric acid. Dried at 100° C., it leaves $2(MgNH_4AsO_4) + OH_2$, which yields on ignition pyro-arsenate, $Mg_2As_2O_7$. The temperature should be raised gradually to avoid any reduction by the escaping ammonia of the arsenic to arsenious oxide

and consequent loss from volatilization. The author determined by a series of the most elaborate experiments (1), the solubility of this salt in the various saline and other solvents with which it is brought into contact during precipitation; (2) the best and most ready methods of drying; (3) the best means of converting the arsenious sulphide into arsenic acid in order to estimate it as ammonio-magnesic arsenate.

He re-dissolved the freshly precipitated arsenate twice in hydrochloric acid, re-precipitating it with ammonia, and allowing it to stand each time for 8 days, before filtering through filters dried at 100° C., and thus repeated with these additional precautions, some of the experiments made by Fresenius * some years ago on the solubility of ammonio-magnesic arsenate.

We refer for the details of these experiments to the original paper, and merely quote the results :—

Solubility in pure distilled water.—One part of the precipitate, dried at 100° C., dissolved in 2652, or one part of the anhydrous arsenate in 2784 parts of water.

Solubility in weak ammonia (one part of ammonia of ·96 sp. gr., diluted with 3 parts of water).—One part of the salt, dried at 100° C., dissolved in 15151, and one part of the anhydrous arsenate in 15904 parts of this aqueous ammonia.

Solubility in a dilute solution of ammonium chloride (one part of the salt dissolved in 60 parts of water).—The amount of arsenate dissolved was determined by removing the arsenic as arsenious sulphide, and precipitation of the magnesia in the filtrate by means of sodium phosphate, and weighing as magnesium pyrophosphate. One part of the salt, dried at 100° C., dissolved in 1321 parts, and of the anhydrous salt in 1386 parts of this dilute solution of ammonium chloride.

Solubility in a concentrated solution of ammonium chloride (one part of the salt in 7 parts of water).—One part of the arsenate, dried at 100° C., required 844·7, and one part of the anhydrous salt 886·7 parts of the solution of ammonium chloride.

Solubility in a solution containing 10 *parts of ammonium chloride,* 10 *parts of ammonia, sp. gr.* ·96, *and* 60 *parts of water.*—One part of the arsenate, dried at 100° C., requires 2879, and of the anhydrous salt 3022 parts of this mixture.

Solubility in a solution of magnesium sulphate (13·3 parts of the crystallised salt dissolved in a litre of water).—One part of the arsenate, dried at 100° C., required 2763, and of the anhydrous salt 2900 parts of this solution.

Solubility in magnesia mixture (one part of $MgSO_4$, one part of AmCl, four parts of ammonia, of sp. gr. ·96, and eight parts of water).—The mixture was diluted with 20 parts of water, and contained 72·58 grms. of the crystallised $MgSO_4$ per litre. One part of the crystallised dried arsenate dissolved in 31483, and one part of the anhydrous salt in 32827 parts of the mixture.

Solubility in sodium arsenate (two parts of the salt in 100 of water).—One part of the dried arsenate dissolved in 4386, and one part of the anhydrous salt, in 4604 parts of the sodic arsenate solution.

Solubility in a 2 *p. c. solution of ammonium nitrate,* rendered slightly ammoniacal.—One part of the arsenate, dried at 100°, required 4184, and one part of the anhydrous salt 4389 parts of the nitrate solution.

Solubility in a 1·5 *p. c. solution of potassium chloride.*—One part of the dried

* Zeitsch. f. analyt. Chem., iii, 206.

arsenate dissolved in 2440, and one part of the anhydrous salt in 2561 parts of the solution of potassium chloride.

Solubility in a solution of ammonium tartrate (prepared by dissolving 3·5 grms. of tartaric acid in weak ammonia, to slight alkaline re-action, and diluting to 250 c. c.).—One part of the dried arsenate dissolved in 1410, and one part of the anhydrous salt in 1422 parts of the tartrate solution.

Solubility in ammonium citrate (prepared by dissolving 2·5 grms. of citric acid in ammonia, to weak alkaline re-action, and diluting to 250 c.c.).—One part of the arsenate, dried at 100°, dissolved in 889 parts, and one part of the anhydrous salt in 933 parts of the citrate solution.

The author observes that ammonio-magnesic arsenate is somewhat soluble in dilute ammonia, but that an excess of magnesia mixture, as well as of sodium arsenate, renders the separation of the precipitate more perfect.

H. Rose has shown that the precipitated ammonio-magnesic arsenate is obtained with six molecules of water of crystallisation by evaporating *in vacuo* over concentrated sulphuric acid. Dried in the water- and air-bath at 100° C. it loses all but a semi-molecule of water, and leaves $2(MgNH_4AsO_4) + OH_2$.

According to Wittstein, good results may also be obtained by cautiously igniting the precipitate, and converting it into pyro-arsenate, $Mg_2As_2O_7$.

The author repeated these experiments, viz.:—drying (1) over sulphuric acid, (2) in a water-bath, (3) in an air-bath, (4) determination as pyro-arsenate, by igniting quickly and intensely, next by igniting gradually, and lastly by igniting in a current of oxygen.

Drying for a considerable time over sulphuric acid led to H. Rose's formula of the salt. Drying in the water-bath left two molecules of the salt in combination with one molecule of water. The author shows that there is no foundation for the assertion that drying at 100° is insufficient, and that a higher temperature is required to obtain this salt of constant composition.

Drying in the air-bath, at a temperature of 100° to 102,° gave equally satisfactory results. When he dried the precipitate, however, at 103° to 110°, till constant, a loss of water was incurred, and this loss was considerably increased by drying at 130°.

In order to avoid the tedious operation of drying the ammonio-magnesic arsenate, it has been repeatedly proposed to ignite, as is done with the corresponding phosphate, and weigh as pyro-arsenate. On igniting portions of the salt dried at 100°, (1) over a small gas jet, (2) over a powerful gas flame, and (3) over the blowpipe, it was found that they lost respectively 3·4 p.c., 4·5 p.c., and 8 p.c. When, however, the salt was ignited, according to Wittstein's method, by first drying the salt at 130° for two hours, then heating cautiously on a sand-bath,

heating by a Bunsen burner for another two hours, then on an iron plate for an hour and a half, then for twenty minutes over the bare flame, and lastly, by heating intensely over the blow-pipe flame, the author obtained satisfactory results. On applying the same operations to the salt dried over sulphuric acid equally good results were obtained. Filters containing small quantities of the arsenate, when soaked with a solution of ammonium nitrate and then deflagrated, showed but a trifling loss. When the dried salt was heated in a current of oxygen, according to Rose's directions,—gently at first, then over a Bunsen burner for a quarter of an hour, and finally very intensely over the blowpipe lamp,—good results were obtained, and the author prefers this method to the extremely tedious method of drying at 100° till constant.

On repeating H. Rose's experiments of reducing ammonio-magnesic arsenate to arsenic with formation of arsenious sulphide (by mixing with powdered sulphur and heating in a current of hydrogen gas and by employing freshly precipitated sulphur), Rose's observation that the arsenic cannot be removed entirely in this manner was confirmed.

By heating the arsenate with acid ammonium sulphate, the arsenic acid is completely reduced to arsenic, which volatilizes. The results obtained by weighing the residuary magnesium sulphate are, however, a little too high, on account of the action of the acid sulphate upon the crucible.

The author next determined whether, as is known to be the case with the ammonio-magnesic phosphate precipitate, any basic magnesium sulphate or pure magnesia is ever carried down by the ammonio-magnesic arsenate, and whether redissolving in hydrochloric acid and reprecipitation with ammonia eliminates any slight admixture of magnesium compounds. He found invariably traces of a sulphate and likewise slight traces of arsenic, as indicated by barium chloride and by sulphuretted hydrogen. We can only quote the results of a number of exhaustive experiments, obtained by precipitating a standard solution of sodium arsenate with varying quantities of the mixture of sal-ammoniac and magnesia salt, viz., that a trifling quantity only of magnesium hydrate or basic magnesium sulphate is precipitated with the arsenate; that especially, a concentrated solution of sal-ammoniac interferes with the precipitation by holding a little of the ammonio-magnesic arsenate in solution, whereas a small excess of magnesia mixture ensures complete precipitation; lastly, that the errors arising from the precipitation of a little basic magnesium sulphate, and from the solubility of the ammonio-magnesic arsenate, nearly neutralize each other, unless an excessive amount of magnesia mixture and sal-ammoniac is employed. The author proposes to allow for every 16

c.c. of the filtrate ·001 grm. of arsenate, and recommends precipitating only once, on account of the solubility of the arsenate in sal-ammoniac.

He arrives at the conclusion that the determination as magnesium pyro-arsenate according to Wittstein, when carefully executed, is as accurate as could well be desired, and far more expeditious than drying at 100° C. For like reasons, he recommends the use of red fuming nitric acid, in preference to all other methods of oxidation (especially after removing the greater part of the precipitated arsenious sulphide mechanically from the filter-paper, and extracting the last traces with ammonia), in order to convert the trisulphide into arsenic acid. The excess of acid is evaporated, and the residue dissolved in a little hydrochloric acid.

III. *Uranic Pyro-arsenate* $(UO)_4As_2O_7$.*

On adding uranic acetate to a solution of an arsenate in water or in acetic acid, a precipitate of uranic arsenate $(UO)_2HAsO_4 + 4HO_2$ is obtained, which loses its water at 120°. In presence of ammonium salts a glutinous yellowish green precipitate of ammonio-uranic arsenate $(UO)_2NH_4AsO_4 + Aq$ is left, insoluble in water and acetic acid, but soluble in mineral acids. On ignition, light yellow uranic pyro-arsenate $(UO)_4As_2O_7$ is obtained. The precipitation is assisted by boiling, and the precipitate subsides more readily on adding a few drops of chloroform to the warm solution, and then boiling up again. The quantitative results being, however, unsatisfactory, the author found that, on ignition, a small portion of the salt is reduced by the escaping ammonia gas. This source of error was to a great extent eliminated by igniting, as in the case of the corresponding magnesium arsenate, with great care, heating first over a sand-bath, then on a hot iron plate, and lastly over the bare flame, or by igniting at once in a current of oxygen.

Excess of ammonia or sal-ammoniac exerted no disturbing influence. Conversion of freshly precipitated arsenious sulphide into arsenic acid by means of potassium chlorate and hydrochloric acid, or by treating with fuming nitric acid and subsequent precipitation in an acetic solution as ammonio-uranic arsenate gave very good results; and since the precipitate could be readily washed out—a desideratum of no small importance—this method of determining arsenic is strongly recommended, and is preferred by the author to all other methods.

W. V.

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* Atomic weight of uranium = 118·8 (Ebelmen).

On the Volumetric Estimation of Iron by Potassium Iodide. By A. SCHWARZER.*

THE author employs, in Mohr's well-known method for the volumetric determination of iron by sodium hyposulphite, a large amount of potassium iodide, which, he asserts, accelerates the reduction so greatly as to render unnecessary Mohr's recommendation to employ hermetically closed vessels for the reaction.

C. G.

A New Volumetric Method for the Estimation of Copper. By FRIEDRICH WEIL.†

THIS depends on the reduction of cupric chloride by stannous chloride in a hydrochloric acid solution: $2CuCl_2 + SnCl_2 = Cu_2Cl_2 + SnCl_4$.

The solutions employed are—

1st. A standard solution of copper containing 15·734 grms. cupric sulphate = 2 grms. copper, per litre.

2nd. A solution of stannous chloride made by dissolving—with the usual precautions against oxidation—6 grms. of tin in 200 c.c. hydrochloric acid, and diluting with freshly boiled distilled water to 1000 c.c. This solution is standardised by means of the cupric sulphate solution.

The solution of cupric chloride to be examined is strongly acidulated with hydrochloric acid, and the standard stannous chloride is run in until decoloration takes place. The completeness of the reaction may be rendered certain by testing a drop with mercuric chloride solution, the formation of calomel indicating the slightest excess of the stannous chloride.

Should iron be present, the author first determines its amount by the permanganate process, and deducts the amount of stannous chloride employed in the reduction of the ferric chloride.

The author closes his paper with analytical results in support of the process.

C. G.

On the Quantitative Estimation of Tannin in Oak-bark. By C. NEUBAUER.‡

THE author has examined numerous methods of estimating the tannin in oak-barks, and has come to the conclusion that a slightly modified form of Löwenthal's method is most to be depended upon.

* J. pr. Chem [2], iii, 139—142. † Dingl. Polyt. J., cxcix, 413—420.
‡ Zeitschr. Anal. Chem. x, 1—40.

The requisites for this method are (1), *A solution of sulphindylate of potassium* (indigo-carmine) 30 grm. to the litre. This solution is to be carefully heated in closed bottles to 70°, whereby its tendency to form confervoïd growths is checked. Only the purest indigo-carmine can be used. 20 c.c. of the solution are diluted to $\frac{3}{4}$ litre, and after the addition of 10 c.c. of dilute sulphuric acid, titrated with potassium permanganate; the colour must change ultimately from greenish to a clear golden yellow, and this change must take place with precision, otherwise the solution is useless. (2.) *Tannin solution.* Chemically pure tannin is dried at 100, and 2 grams are dissolved in 1000 c.c. It is pointed out that the differences between chemists in their analyses of oak-bark are probably due in many cases to their having operated with standard solutions of tannin of different degrees of purity. For testing the purity of commercial tannin the author recommends Hammer's process, viz., the observation of specific gravity before and after the tannin has been absorbed and removed from solution by rasped hide. (3.) *Solution of potassium permanganate* containing 10 grm. of pure crystallised potassium permanganate in 6 litres of water. (4.) *Decinormal solution of oxalic acid* may be used for titration of the permanganate, instead of the tannin solution. This would contain 6·3 grm. to the litre, and according to the author's experiments will correspond to a tannin solution containing 4·157 grm. tannin per litre. This weak oxalic acid does not keep well unless treated as recommended for the indigo-solution, viz., heated in closed vessels to 70° for some time. (5.) *Pure animal charcoal* exhausted with hydrochloric acid, and well washed until the chlorine reaction disappears; it is preserved under water. (6.) *Pure dilute sulphuric acid.*

Standardizing.—To 20 c.c. of the indigo solution diluted with $\frac{3}{4}$ litre of water are added 10 c.c. of the sulphuric acid, and then the permanganate solution is slowly run in, the liquid being constantly and vigorously stirred; the blue colour passes through various shades of green, turning to a slightly greenish-yellow, and ultimately a bright golden yellow; this change of colour is the terminal point of the reaction, and as it is not easy to see the pink colour of the permanganate in the yellow solution, the disappearance of the green must be carefully noted. The operation is now to be repeated with a fresh portion of the indigo solution and 10 c.c. of the tannin solution, the difference between the amounts of permanganate used is the measure of the tannin. 20 c.c. of the indigo solution should always require at least as much permanganate as 10 c.c. of the tannin solution; it is better that they should require half as much again.

Titration of an Oak-bark extract. This is performed as above described. If one litre of extract has been prepared from 20 grams of oak-bark powder, from 10 to 20 c.c., according to the quantity of

tannin present, are employed in the titration. Repetitions of the analysis give closely concordant results. The tannin used in titration being obtained from the gall-nut is not identical with that contained in the oak-bark, of which more hereafter. Again, the oak-bark tannin is not a pure substance; but though the extract of the oak-bark contains many other matters besides tannin, which reduce permanganate, still the action of most of these matters is slow, and their effect consequently small. The author quotes Buchner (*Dingler's Polyt. Journ.*, clxxxiv, 345), who has studied the action of permanganate on the pectic acid obtained from oak-bark extract. Buchner did not obtain this body white or free from tannin, but by the use of animal charcoal the author succeeded *in precipitating not only all colour from the aqueous extract, but also the whole of the tannin.* To obtain the pectic acid, 700 c.c. of bark extract (20 grms. to the litre) were evaporated, and after cooling, the concentrated solution was precipitated by alcohol. The precipitate was washed with alcohol, dissolved in water, treated with a sufficient quantity of animal charcoal, then filtered, greatly concentrated on the water-bath, again filtered, and finally precipitated with alcohol. The colourless precipitate thus obtained, after being collected on a filter and washed with alcohol, dissolved in water to a colourless solution; this by long boiling was freed from alcohol, and then made up to 100 c.c. In this solution neither iron acetate nor a mixture of sodium acetate and iron chloride caused a dark brown precipitate, as Buchner obtained with his impure precipitate. 10 c.c. of this solution contained all the pectin from 1·4 grm. of oak-bark. The author shows conclusively that this large amount of pectin does not seriously affect the titration with permanganate and indigo; for instance, in one example brought forward by the author, the effect of the pectin would have been to raise the apparent amount of tannin from 100·00 to 101·65.

The author then shows that in the aqueous extract of oak-bark, animal charcoal, while precipitating the tannin and colouring matter, does not precipitate the pectin, and on this fact he bases his modification of Löwenthal's process.

The author takes three equal portions of the extract, one is titrated as above; to the two others equal quantities of animal charcoal are added. After standing for a few moments a sample from one of them is filtered and tested by adding to it, first sodium acetate, and then ferric chloride. If the tannin reaction can no longer be detected, the other portion which has been treated with animal charcoal is filtered, the charcoal washed, and the filtrate titrated as before. The amount of permanganate required by this is subtracted from that required by the portion of the extract not treated with animal charcoal. The difference is the measure of the tannin. The author points out that

there may be matters present which would reduce permanganate and be at the same time precipitable by charcoal; were gallic acid present, it would belong to this category. Neubrand in 1869 published a paper containing some analyses of oak-bark, in which he stated that he had detected and estimated gallic acid, notwithstanding that Stenhouse, who operated on 6 to 8 lbs. of oak-bark, had in 1843 failed to detect this body. Stenhouse, however, readily detected it in Sumach, Valonia, or Dividivi.

Testing the Method.—The author now considers the question raised by Gauer and Hallwachs: Is the decomposition of the tannin constant in solutions of different degrees of concentration and mixtures? He publishes eleven determinations made under varying circumstances which prove that within tolerably wide limits the results are constant notwithstanding variations in the concentration, &c., also that mixtures of different tannin solutions and bark extracts yield numbers fairly in unison with those calculable from the volumes of the solutions employed, and their known behaviour when titrated before mixture. Some of the quoted experiments are by the author's assistant, Herr Rupprecht.

The author here quotes, from a paper of Neubrand, some remarks to the effect that what is needed in a method of estimating the value of barks containing tannin, is not an absolute measure of the latter, but a relative measure only, and a measure which shall be constant for the same bark, even when the estimation is made by different chemists. To prove that the modified method of Löwenthal recommended by the author presents these advantages, he gives a set of analyses made by four different chemists, the numbers obtained corresponding in a satisfactory manner. It is, however, to be noted that it is only when the bark extracts are made in precisely the same manner that corresponding results are obtained: the quantity of water commonly recommended, viz., $\frac{3}{4}$ litre to 20 grams of bark (boiled for three-quarters of an hour) is so small as to render it hardly possible to extract the bark completely. The next question is, does the boiling of the bark in contact with the air affect the result by oxidizing the tannin? Three experiments were made on the same oak-bark by boiling three separate portions of 20 grams each for, respectively one, two, and three hours with $\frac{3}{4}$ litre of water; the extracts were then titrated: they gave respectively 7·34, 7·17, and 6·93 per cent. tannin. A second set of experiments on another bark gave similar results, so that this source of error was not serious; moreover, it is possible to exhaust the bark almost perfectly in the cold.

Tannin of Oak-barks.—This substance differs from the tannin of gall-nuts in many respects, and, therefore, the question arises, are we justified in estimating the tannin in oak-bark by comparison with a

tannin-solution obtained from the tannin in gall-nuts? Obviously we are not, in the strict sense of the words, but simply as a relative measure such a method is permissible.

The author quotes some experiments of R. Wagner, who endeavoured to determine the atomic weight of oak-bark tannin, and to substitute this for the gall-nut tannin as the basis of the bark analysis; however, Wagner appears not only to have failed in his object, but to have arrived at some perfectly incomprehensible results. The opinion of the author obviously is, that Wagner's research is not in any sense to be depended upon.

The Löwenthal method, as modified by the author, is not applicable to such materials as contain gallic acid in addition to oak-bark tannin, because the gallic acid is oxidized precisely as the tannin would be, and is also precipitated by animal charcoal. Sumach belongs to this class.

Wagner's Method and Buchner's Research.—The author shows that the principle of Wagner's method, viz., the insolubility of the compound of cinchonine and oak-bark tannin is unsound, inasmuch as the filtrate from the precipitate, even when the precipitant has been added in excess, as shown by the indicator recommended by Wagner, still contains tannin, a fact readily proved by the addition of a solution of glue, or by the iron test. Moreover, sulphuric acid, according to the author, readily dissolves the precipitate, and does not, as stated by Wagner, increase its insolubility. The author endeavoured to substitute acetic acid for sulphuric acid; but though the compound of tannin and cinchonine is less soluble in this acid than in sulphuric acid, it is still very notably soluble; it is also notably soluble in water. The author summarises his examination of Wagner's method and Buchner's research to the following effect. Wagner's method yields results absolutely false and useless, and the whole of the results obtained by Buchner according to this method, must be described as entirely worthless, and as having tended in no small degree to confuse the forest-officers (Forstbeamten), and destroy their belief in the results of chemistry in this matter.

Löwe states that pectin interferes with the accuracy of the tannin estimation, and therefore proposes to evaporate the extract of the bark to dryness, take up with alcohol, again evaporate to dryness, dissolve the residue in water, and estimate the tannin in this solution. Both Buchner and the author have, however, observed that the alcohol will not extract the whole of the tannin, and that, therefore, this modification is not available. The repeated evaporations to dryness, moreover, expose the tannin to the danger of oxidation. Besides, the use of animal charcoal, as described above, does away with the necessity of the treatment with alcohol.

Preparation of Oak-bark Extract for Analysis.—The author here insists with great detail on the necessity of taking large samples, having them crushed in an ordinary tan-mill, then taking a portion (about 2 lbs.) of this crushed bark, and preparing it for analysis by finely grinding it in a specially constructed steel mill. He next quotes some experiments to show that it is absolutely necessary to dry the bark before estimating the tannin in it, as the amount of water retained by the bark varies greatly with the state of the weather; he, therefore, dries his samples in the water-oven. After describing the methods of making the extract recommended by Fresenius, Hartig, Lipowitz, and Mittenzwei, the author summarises his own experience by stating that the results of the analysis will differ with the method of extraction adopted, and that beyond all doubt, one portion of the tannin is more easily extracted by water than the other.

The method recommended by the author is to exhaust 20 grm. of the finely powdered bark with 1 litre of cold water, using Real's press; the partially extracted bark is then boiled for three-quarters of an hour with $\frac{3}{4}$ litre of water without the addition of acids, and both extracts are separately titrated.

A further amount of tannin can be obtained from the residue exhausted as above described, by boiling with more water, and a still further amount by boiling with acidulated water, but it may be doubted whether the tannin so extracted is practically useful to the tanner.

The following table gives the amounts of tannin, as indicated by the author's method of analysis, in various extracts, obtained from the same sample of bark, by different methods:—

		Per cent.
(1.) By one boiling with water (20 grams of bark boiled three-quarters of an hour with $\frac{3}{4}$ litre of water)		8·80
(2.) By treatment in Real's press with cold water (20 grams to 1 litre)	*a.*	8·34
	b.	8·63
	c.	8·17
(3.) The same as (2); 20 grams to 4 litres		9·23
(4.) The same as (3), but residue of bark boiled three-quarters of an hour with $\frac{3}{4}$ litre of water as in (1)		9·97
(5.) By treatment in Real's press with cold water (20 grams to 1 litre), residue of bark boiled three-quarters of an hour with $\frac{3}{4}$ litre of water		10·27
(6.) Same as (5), but residue twice exhausted with boiling water		10·27

(7.) Same as (6), but in addition the thrice exhausted residue was again treated with $\frac{3}{4}$ litre of water, and 10 c.c. dilute phosphoric acid. . 10·47

E. T. C.

On the Chemical Detection of Curarine. By KARL KOCH.*

THE author follows essentially the method of Dragendorf. The principal organs are cut up fine, and rubbed to the consistency of a thin paste with distilled water, and then dilute sulphuric acid is added to distinct acid reaction. The acid watery extract, after 24 hours' digestion at 40°—50° C., is strained off; the residue again digested as before for another 24 hours; and the two portions of extract are evaporated on the water-bath to the consistency of a syrup, which is then mixed with four times its volume of alcohol, and allowed to digest, with repeated agitation, for 24 hours. The precipitated albumin, &c., is removed by filtration, and the alcohol by distillation; then, as the residue in the retort cools, the separated fat is removed by a wet filter, and this last filtrate is shaken with half its volume of amyl alcohol for two hours. This last removes from the acid liquid many impurities (curarine is not soluble in amyl alcohol). After separating it, the watery liquid is agitated with a fresh portion of amyl alcohol, and, after the separation of this, it is concentrated to a syrup and mixed with two ounces of alcohol of 95°, then filtered; the filtrate is treated with a few drops of baryta water; the excess of the baryta is removed by carbonic acid; the liquid again filtered, the alcohol evaporated; and the residue redissolved in 10—15 c.c. of water.

Koch then describes such modifications of the work as are useful in examining the blood, urine, fæces, &c.; but for these we must refer to the original paper. When the solution which should contain the curarine, has been obtained, the author, like most other toxicologists, gives the greatest weight to the physiological reactions, but, nevertheless, describes certain chemical reactions as having more or less value.

·00006 grm. curarine treated with $\frac{1}{4}$—$\frac{1}{2}$ c.c. concentrated sulphuric acid gives an immediate red coloration, which becomes darker on standing, and, after four hours, passes into rose-red, which colour remains for several days. The acid must be the monohydrate. Dilute sulphuric acid (1 : 50) when evaporated with curarine on the water-bath, shows no action at first, but when the mixture becomes almost dry it first takes a reddish, and a short time afterwards purple, and lastly passes into black. If chromate of potash is added to the purple-red solution, the colour immediately disappears without showing any blue.

* Chem. Contr., 1871, 219.

Concentrated sulphuric acid and chromate of potassium give the same reaction as with strychnine, only the passage from blue into violet and cherry-red is quicker, and the last colour is far more permanent (it lasts from several hours to some days).

Curarine is slightly, but slowly, soluble in chloroform; it diffuses through parchment paper very slowly; it is insoluble in amyl alcohol, benzene, and petroleum ether. The rest of the paper is physiological.

C. H. G.

Testing Cochineal. By J. M. Merrick.*

The author having frequently had occasion to test samples of cochineal, in order to ascertain their comparative colouring powers, recommends the following process for their examination. About two grams of the finely powdered sample are boiled in a flask with 750 c.c. of water for an hour; the decoction is then filtered through a dry paper filter, and left to cool. [It is not stated to what extent the 750 c.c. may be reduced by boiling, or whether the filter is to be washed, and the liquid made up to a known volume.] To test this solution, 50 c.c. are measured with a pipette into a 200 c.c. flask, and a *weak* solution of potassium permanganate is added from a burette; the flask being well shaken after the addition of every 10 c.c.

So much permanganate solution is added, that the cochineal extract shall be changed from its original colour to a pink of the very faintest shade, almost yellow, in fact, but never reaching a full yellow. This pink shade should be persistent, that is, it should not turn yellow after standing 15 minutes; with a little practice it will be found very easy to obtain the tinge, which shows that the colouring matter is almost, but not quite destroyed.

The number of c.c. required by any two samples, A and B, having been thus determined, the relative amount of colouring matter in each is readily calculated, since it is directly proportional to the quantity of permanganate respectively consumed. It is a good plan, when several samples are compared at the same time, to make a final trial, by measuring 50 c.c of each solution into a flask, and then to run in the previously ascertained amount of permanganate at once; on allowing the whole to stand for ten minutes, and then examining the shades of colour in each, they will, if the analysis has been properly conducted, be found in every instance to correspond exactly.

The author states that the proposed method has proved, according to his own experience, not only much simpler than that which is based

* Pharm. Jour. Trans. [2], I, 906.

upon dyeing strips of mordanted woollen stuffs, but also more accurate in its results than when chloride of lime is employed as the bleaching agent.

J. W.

On the use of the Spectroscope for the quantitative Estimation of Colouring Matters. By K. VIERORDT.*

VIERORDT proposes to use for this purpose a slight modification of the ordinary spectroscope. As usually made, the slit consists of one movable and one fixed knife-edge; the movable plate is to be divided into two parts, an upper and a lower half, each of which is provided with a fine micrometer screw, which is graduated, that the width of the slit may be accurately known. It is found convenient to have the eye-piece of the observing telescope fitted with an arrangement by which the whole of the spectrum can be shut out, with the exception of the particular part under observation.† If the two halves of the slit are of equal width, the two spectra will, of course, be of equal intensity; but if a coloured glass or solution be placed in front of one part of the slit, this equality will be destroyed; by altering the width of the open half of the slit, the two spectra, so far as one particular region is concerned, may be again made equal. The particular part of the spectrum used will depend on the nature of the colour. If the absorption of the colour is very strong, a smoked glass of known intensity may be used before the open half of the slit. The strength of the absorption will be given by the comparative widths of the two halves of the slit. In this way, if the absorption co-efficient of a solution of known strength of a pure colouring matter is known for any particular region of the spectrum, the concentration of any solution of it may be easily found by measuring in the above manner the extinction of the light caused by a layer of absorbing medium of any definite thickness.

A. P.

The Areometric Analysis of Beer. By A. METZ.‡

THE beer is first freed, as far as possible, from carbonic acid by shaking, and its specific gravity at 14° R. determined by a delicate areometer. The instrument employed by the author gives exact readings to the

* Deut. Chem. Ges. Ber., iv, 327.

† The details of this arrangement are given in a work "On the application of Spectral Analysis to the Measurement and Comparison of the Intensity of Coloured Light," (Laupp, Tübingen.) by K. Vierordt.

‡ Chem. Centr., 1871, 316, from Polyt. Centr. xxv, 191.

fourth place of decimals. 500 c.c. of the beer is next boiled down to about one-third, and after cooling is again made up to the original volume. From these two determinations the contents of the beer in alcohol and extract, can be calculated by the help of Balling's tables. The author gives an example of the calculation in full; it is too long to extract entire, and does not admit of condensation.

C. H. G.

Technical Chemistry.

Red Colour-printing with Artificial Alizarin. By ARMAND MÜLLER.*

A RED similar in tint and purity to Turkey red was obtained by the author from anthracene-alizarin by means of direct printing.

The pigment (containing much purpurin) in a pasty form, and having 25 per cent. dry material, is dissolved in boiling spirit in the proportion of 1 : 5, and immediately mixed with a concentrated solution of aluminium chloride of which the pure Al_2Cl_6 is to the weight of the colouring matter as 1 : 3. The liquid is thickened with a little tragacanth, and for every half litre of this mixture 30 c.c. of a solution of the best olive oil in sulphuric acid and a little spirit (15 : 1 : 15) is stirred in. This solution must be as thin as possible, but must be thick enough to withstand the capillarity of the cloth. The cotton cloth with which this colour is to be used, is first impregnated with a solution of aluminium acetate of about 8° B., and after drying and two days' airing, is taken through a soap-bath containing 30 grm. Marseilles soap to the litre of water, then well washed out and dried.

The cloth printed with the above mixture is now exposed to strongly ammoniacal steam at a moderately high pressure, taken through a weak soap-bath, washed in a stream and taken through the following series of liquids:—(1) cold nitric acid, 3 c.c. to 1 litre water; (2) washed in stream; (3) cold nitric acid, 5 c.c. to 1 litre water; (4) tin salt, ½ grm. tin salt to 1 litre water at 30° C. — 5) washed in stream; (6) liquor of Javelle, 15 c.c. of 8° B. to 1 litre water cold; (7) thorough washing. The colour is now thoroughly developed and behaves to light, air, and soap like ordinary Turkey red. In preparing the aluminium chloride (by addition of barium chloride to aluminum sulphate) it is absolutely necessary to avoid an excess of the barium salt.

C. H. G.

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* Chem. Centr., 1871, 304.

Upon a Combination of the Bessemer and Martin Processes. By ALBERT BRUNNER.*

THE author points out the advantages to be derived from a combination of these two methods for the manufacture of cast steel. He recommends the employment of Siemens's furnaces for melting old rails, sheet-scrap, &c., as well as pig itself, and makes some suggestions as to the position of the furnaces, and the mechanical arrangements required for working the processes simultaneously.

C. G.

On the Reduction of certain Metals from their Solutions by Metallic Sulphides, and the Relation of this to the occurrence of such Metals in a Native State. By WILLIAM SKEY (Chem. News, xxii, 232).

Roasting of Sulphuretted Ores. By HASENCLEVER and HELBIG (Chem. Centr., 1871, 267).

Analysis and Composition of the Leads of the Upper Hartz. By W. HAMPE (Chem. Centr., 281).

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* Chem. Centr., 1871, 253.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

SESSION 1870–71.

November 3rd, 1870.

Dr. Williamson, President, in the Chair.

C. W. Siemens, 3, Great George Street, Westminster; David Howard, Stamford Hill, N.; and John Muter, 289, Kennington Road, S.; were elected Fellows.

The following papers were read:—

"On the Production of the Sulphates of the Alcohol-radicals by the Action of Sulphurous Acid:" by E. T. Chapman.

"On the Determination of Sulphur in Cast Steel:" by A. H. Elliott.

"On the Composition of the Hyposulphites:" by E. A. Letts.

November 17th.

Dr. Williamson, President, in the Chair.

The following papers were read:—

"Mineralogical Notices:" by Nevil Story-Maskelyne and Walter Flight.

"Note on the Oxides of Nitrogen:" by E. T. Chapman.

December 1st.

Dr. Williamson, President, in the Chair.

R. Barklie, 15, Hopeton Street, Belfast; Dr. Ogg, Madras; H. E. Armstrong, 8, Belmont Hill, Lee; W. L. Carpenter, Clifton,

Bristol; T. Farries, 16, Coleman Street; J. Dewer, Edinburgh; R. Mallet, Westminster Chambers, Victoria Street; and J. M. Crafts, Cornell University, Ithaca, N.Y.; were elected Fellows.

The following paper was read:—

"On some Derivatives of Anthracene:" by W. H. Perkin.

December 15th.

Dr. Frankland, Vice-President, in the Chair.

R. Koma, University College; J. F. Stark, Glasgow; and G. T. Atkinson, Clifton College; were elected Fellows.

The following papers were read:—

"On some New Derivatives of Coumarin:" by W. H. Perkin.
"On the Formula of Glyoxylic Acid:" by H. Debus.

January 19th, 1871.

Professor Odling, Vice-President, in the Chair.

E. Potts, High Street, Sunderland; R. J. Moss, 2, Fortfield Terrace, Dublin; J. Moss, 17, Bloomsbury Square; H. T. Brown, Burton-on-Trent; and R. Banister, Somerset House; were elected Fellows.

The following papers were read:—

"On the Action of Sulphuric Acid on the Natural Alkaloïds:" by H. E. Armstrong.
"On the Origin of Nitrates in Potable Waters:" by C. Ekin.

February 2nd.

Dr. Williamson, President, in the Chair.

J. R. Tustin, 9, Paragon, Blackheath; W. Gowland, 4, Olive Terrace, Stretford, Manchester; R. J. Friswell, 74, Great Russell Street, Bloomsbury; B. J. Grosjean, 97, Euston Road; and R. F. Humiston, University Heights, Cleveland, Ohio; were elected Fellows.

The following paper was read:—

"On the Development of Fungi in Potable Waters:" by Dr. Frankland.

February 16th.

Dr. Williamson, President, in the Chair.

W. D. Herman, St. Ann's, St. Helen's, Lancashire; W. W. Houlder, Southall, Middlesex; G. Lockyer, jun., 15, Grove Boltons, Brompton; J. E. Mayer, Cambridge Terrace, Junction Road, Kentish Town; R. Meldola, 21, John Street, Bedford Row; M. M. P. Muir, 12, Woodlands Terrace, Glasgow; W. J. Reynolds, 24, Mare Street, Hackney; W. Smith, Glasgow; T. E. Thorpe, Glasgow; and W. J. Lockyer, Pembroke Villa, Elgin Park, Bristol; were elected Fellows.

The following papers were read:—

"On the Effects of Pressure on the Absorption of Gases by Charcoal:" by John Hunter.

"On the Solubility of the Phosphates from Bone-ash in Water containing Carbonic Acid:" by Robert Warington.

March 2nd.

Dr. Williamson, President, in the Chair.

J. J. Nicholson, Sunderland; A. H. Mason, 317, Upper Parliament Street, Liverpool; W. H. Hudleston, 23, Cheyne Walk, Chelsea; and G. D. Harding, Askam-in-Furness, Lancashire; were elected Fellows.

The following papers were read:—

"On the Distillation and Boiling Point of Glycerin:" by T. Bolas.

"On the Action of Heat on Silver Nitrite:" by E. Divers.

March 16th.

Dr. Williamson, President, in the Chair

C. H. Piesse, 1, Merton Place, Chiswick, was elected a Fellow.

The following paper was read:—

"On the Examination of Glucose-containing Sugars:" by C. H. Gill.

March 30th.

Dr. Williamson, President, in the Chair.

Anniversary Meeting. (See page 609.)

April 6th.

Dr. Frankland, President, in the Chair.

C. E. Groves, 17, Rodney Street, Pentonville; L. T. MacEwen, Lombard House, 56, Lombard Street, E.C.; E. W. T. Jones, Pennfields, Wolverhampton; F. Coles, 248, King's Road, S.W.; and J. S. Shorter, Lawn House, Holloway; were elected Fellows.

The following papers were read:

"On Burnt Iron and Steel:" by W. Matthieu Williams.

"On the Formation of Sulpho-acids:" by H. E. Armstrong.

"On a Water from the Coal Measures at Westville, Nova Scotia:" by Prof. How.

April 20th.

Prof. Odling, Vice-President, in the Chair.

C. C. Grundy, Bankfield, near Bury, Lancashire; S. B. Lee, Sidney Sussex College, Cambridge; G. Sutcliffe, 34, East View, Preston; and W. Ward, Sheffield Moor, Sheffield; were elected Fellows.

The following paper was read:—

"On some saline Compounds of Cane Sugar:" by C. H. Gill.

May 4th.

Dr. Warren Delarue, Vice-President, in the Chair.

W. H. Darling, 126, Oxford Street, Manchester; C. S. Cross, 4, Hamilton Terrace, Highbury; J. Schweitzer, King's Road, Brighton; W. A. Smith, Rascliffe Crescent, Huddersfield; R. S. Best, Moor House, Goole; and G. H. Ogston, Mincing Lane; were elected Fellows.

A lecture was delivered, "On the Productive Powers of Soils in relation to the Loss of Plant-food by Drainage:" by Dr. Voelcker.

May 18th.

Dr. Frankland, President, in the Chair.

T. Greenish, 20, New Street, Dorset Square; and J. E. Mayall, Hove Place House, Brighton; were elected Fellows.

The following papers were read:—

"On a New Double Salt of Thallium:" by R. J. Friswell.

"On the Action of Nitric Acid on Dichlorophenolsulphuric Acid:" by H. E. Armstrong.

June 1st.

Dr. Frankland, President, in the Chair.

H. Durham, 24, Gordon Road, Stoke Newington; E. Neison, 37, Fellows Road, Eton Park, N.W.; Huskisson Adrian, 52, Cumming Street, N.; and George Martineau, Walton-on-Thames; were elected Fellows.

A lecture was delivered "On Ozone," by Dr. Debus.

June 15th.

Dr. Frankland, President, in the Chair.

M. J. Salter, 26, Horton Road, Dalston; C. Willmore, Queenwood College; J. Bottomley, 4, Iswell Terrace, Lower Broughton, near Manchester; H. R. Procter, Clementhorpe, North Shields; and B. Finkelstein, Chemist at St. Rollox, Glasgow; were elected Fellows.

A lecture was delivered "On an Experimental Inquiry as to the Action of Electricity upon Oxygen:" by Sir B. C. Brodie.

Anniversary Meeting, March 30th, 1871.

Dr. Williamson, President, in the Chair.

The following Report was read by the President:—

Gentlemen,

I feel much pleasure in congratulating you on the rapidly increasing prosperity of our Society and the enlargement which has taken place in its sphere of usefulness. For on the one hand the number of our

Fellows continues to show a most satisfactory increase, and on the other hand your Council has made arrangements for carrying out the system of Monthly Reports which has been from time to time in contemplation. It was hoped that the Chemical Society of Paris might from the first co-operate with us in the preparation of these monthly reports, but circumstances beyond their control have prevented the sister Society from joining us in the beginning of this year. Deeming it undesirable to delay the commencement of the reports, your Council still look forward to the future co-operation of the Paris Society in their preparation.

You are aware that the present available income of the Society was not considered to be sufficient to defray the additional expense of writing and printing these reports, and I have the pleasure of informing you that contributions to the extent of £1,175 have been promised by members of your body, towards supplying the deficit during the first five years of the appearance of the reports. The British Association has, moreover, granted us the sum of £100 for this year in aid of the undertaking. We hope that in five years the funds of the Society may have sufficiently increased to enable us to pay the whole expense of the reports, and that their publication will be valued by the members of our Society, and will promote the advancement of our science wherever the English language is read.

The next number of our Journal, which I hope to see in a few days, will be the first to contain the Monthly Reports, in addition to the original papers contributed to the Society.

At the last Anniversary Meeting we numbered 551 ordinary members and 36 foreign members. Of the former, six have withdrawn from the Society, and we have lost five by death. On the other hand, 42 new members have been elected into the Society, so that we now number 582 ordinary members.

The deceased members are, viz.:—Mr. George Jolley, Dr. W. A. Miller, Dr. Aug. Matthiessen, Dr. J. S. Muspratt, and Mr. W. W. Rouch: and it is also my painful duty to record the death of two of our foreign members, viz.:—Professor Gustav Magnus, and Professor Weltzien.

Heinrich Gustav Magnus was born at Berlin on the 2nd of May, 1802. From an early age he exhibited peculiar aptitude for the pursuit of the exact sciences. He studied at the University of Berlin, and took his Doctor's degree in 1827. His first researches were made in Mitscherlich's laboratory; he worked with Berzelius, at Stockholm in 1828, and afterwards, went to Paris, where he frequented the

laboratory of Gay-Lussac, and prepared himself for the important researches which he made some years later on gases. On returning to Berlin in 1831, he began his career as teacher in the capacity of Privat-Docent; in 1834 he was elected Extraordinary Professor, and in 1845, Ordinary Professor of Physics and Technology in the University.

In 1825 he published in Poggendorff's Annalen, a very interesting memoir on the property possessed by iron, cobalt, and nickel reduced from their oxides by ignition in hydrogen, of taking fire spontaneously in the air at ordinary temperatures. In 1828 he discovered the ammoniacal platinum salt, commonly known as the "Green Salt of Magnus," which has served as the point of departure for a whole series of compounds containing platinum and the elements of ammonia. In a research made conjointly with Ammermüller, he discovered Periodic acid. He also discovered Ethionic and Isethionic acids; analysed a large number of minerals; and discovered the singular property possessed by certain crystallised silicates, such as garnets, of undergoing a considerable decrease of density by fusion.

His most important researches, however, related to Molecular Physics and to Heat. His earliest physical memoir entitled "Researches on Capillarity," is rather a study of the diffusion of gases and their passage through cracked tubes. He subsequently published some interesting observations on evaporation in capillary tubes, and on the boiling of mixed liquids. On this latter point he showed, as indicated by theory, that ebullition takes place at the temperature at which the sum of the tensions of the mixed vapours is equal to the atmospheric pressure, and therefore at a temperature a little below the boiling point of the most volatile liquid. He observed also that this condition is not completely realised when the more volatile of the two liquids is situated below the other, the mixture in this case becoming over-heated, and entering suddenly into ebullition with a violent explosion.

About the same time, that is to say in the earlier years of his professional career, Magnus published his interesting researches on the Gases of the Blood. The theory of respiration most generally received up to that time was that of Lavoisier, according to which the combustion of the blood was supposed to take place completely at the moment when it comes into contact with the air of the lungs. Magnus however found, both in arterial and in venous blood, considerable quantities of oxygen, nitrogen, and carbonic acid, the oxygen amounting to between $\frac{1}{3}$ and $\frac{1}{2}$ of the carbonic acid in arterial, and between $\frac{1}{4}$ and $\frac{1}{5}$ in venous blood. He thence concluded that the combination of oxygen with the carbon of the blood does not take place immediately in the lungs, but that the oxygen is absorbed by the

arterial blood, and transported to the capillaries, where it is employed in the combustion of the various substances eliminated by the organism; and that the carbonic acid resulting from this combination, is likewise absorbed, carried forward by the venous blood, and expelled on its arrival in the lungs. This is the theory now generally adopted.

The researches in which Magnus displayed the highest degree of his experimental talent are those which relate to the Expansion of Gases. The experiments of Gay-Lussac, corroborated by those of Dulong and Petit, had led to the conclusion that all gases have the same coefficient of expansion, and that between 0° and 100°, the volume of every gas expands by 0·375 of its volume at 0°. This law was universally received, as one of the best established results of experiment, till Rudberg, forty years after the publication of Gay-Lussac's research, took up the investigation and found for the expansion coefficient of air, the number 0·3646. To reconcile this difference on so important a point, further experiments were undertaken about the same time by Magnus and by Regnault, the results of the former being communicated to the Berlin Academy of Sciences, on the 25th of November, 1841, and those of the latter to the Academy of Sciences at Paris, on the 13th of December of the same year. Magnus, having first repeated the experiments of Gay-Lussac, which consisted in observing the expansion under constant pressure of a quantity of air enclosed in a flask by a small column of mercury, which moved backwards and forwards in the capillary neck according to the change of volume of the air, soon found that this method is affected by several causes of error. Nevertheless, he obtained, as the mean result of his experiments, the number 0·369 instead of 0·375, the difference being probably due to more complete dessication of the air in Magnus's experiments. He then resorted to the method of Rudberg. His apparatus consisted of a tubulated glass vessel communicating with a manometric apparatus, and enclosed within a triple envelope of iron plate, in the interior of which any desired temperature could be maintained. By increasing the pressure, the volume of the gas at 100° could be brought back to that which it occupied at 0°. The coefficient of expansion was then deduced from the observed difference of pressure by a very simple equation founded on Mariotte's law. The value thus obtained for the expansion-coefficient of air was 0·366508, being a little higher than that given by Rudberg. By experimenting in the same manner on different gases, Magnus obtained for hydrogen an expansion-coefficient somewhat less, and for carbonic anhydride and sulphurous anhydride coefficients somewhat greater, than that of air, viz.:—

Hydrogen.	Carbonic anhydride.	Sulphurous anhydride.
0·365659	0·369087	0·385618

Regnault made four series of experiments, the first two in which both the volume and the pressure were made to vary, giving for air the two nearly equal values, 0·36623 and 0·36633; while the third and fourth gave for the expansion-coefficient of air, at constant volume and variable pressure, the values 0·36679 to 0·36650. By operating on different gases, Regnault obtained numbers nearly identical with those of Magnus. The result of the experiments of these two philosophers was, therefore, to replace the coefficient 0·375 by 0·366 for air, and to show that different gases have unequal rates of expansion.

The difference between the values found by Gay-Lussac on the one hand, and by Rudberg, Magnus, and Regnault, on the other, arose mainly from the fact, that in the earlier experiments, a layer of moisture had remained on the inner surface of the vessel which contained the gas, and, being converted into vapour as the temperature was raised, had increased the apparent expansion. Now an effect of the same kind might be produced by the condensation of the gas itself, which was the subject of experiment. To ascertain whether this was the case, Magnus made two determinations of the expansion-coefficient the same gas, namely sulphurous anhydride, the surface of the glass relatively to that of the air being enormously increased in one case by the introduction of a number of fragments of glass rod. Under these circumstances, the coefficient of expansion of the gas was found to be considerably greater, and it was thus shown that gases condense at low temperatures on the surface of solid bodies.

In 1860 and 1861, Magnus published an important memoir on the Transmission of Heat through Gases by Conduction and Radiation. By placing a thermometer in a glass vessel heated from above and filled successively with different gases and vapours, he found that the thermometer became heated to different degrees in different gases, and less in any of them, with one exception, than in a vacuum. Hence he concluded that gases do not transmit heat, or only to a very slight extent by conduction, and that they absorb a considerable quantity of that which passes into them by radiation. Hydrogen, however, exhibits an exception to this law, at least so far as regards the first part, the thermometer becoming more strongly heated in this gas than in a vacuum, and to a higher degree in proportion as the gas is more condensed, although the proportion of radiant heat absorbed by hydrogen is the same as that absorbed by air, nitrogen, or oxygen: hence it appears that hydrogen conducts heat like a solid body. This conductivity of hydrogen is exhibited when it is enclosed in a substance of low conducting power, such as cotton-wool, as well as when currents are free to form within it.

The experiments of Magnus on the Diathermancity of Gases were made with an apparatus consisting mainly of a large glass vessel,

heated from above, and containing the gas, together with a thermo-electric pile to measure the amount of radiation. He found that all gases absorb radiant heat, and in greater proportion as they are more condensed. The least absorbent are air, nitrogen, and oxygen, then, but with very little difference, hydrogen. Amongst colourless gases, the most absorbent are ammonia and ethylene. The differences between the absorbent powers of the several gases for radiant heat vary with the source of heat employed, the most striking differences being obtained with a source of non-luminous heat having a temperature of 100°. Lastly, according to Magnus, vapour of water, so long as it is in the state of transparent gas, exerts no appreciable absorption on radiant heat. On this point his results are in direct contradiction to those of Tyndall, from whose experiments it appears that the vapour of water contained in the air absorbs 40, 50, and even 60 times as much radiant heat as the air itself. The opposition in the results obtained by those two philosophers has given rise to considerable discussion, but it has not yet been satisfactorily explained.

Magnus made a number of other very interesting experiments on Radiant Heat. He studied especially the variation in the emissive power of a body according to the degree of polish of its surface, and showed that the increase of this emissive power, produced by roughening the surface, depends, not on a diminution of density in its superficial stratum, but on the discontinuity of this stratum. He found, moreover, that the increase of emissive power in roughened platinum does not extend to all the rays of heat, but only to those situated in or near the red.

A short time before his death, he published a memoir on the Absorption and Reflection of Heat by bodies at low temperatures, in which he showed that different bodies at temperatures near 100° emit, absorb, and reflect very different calorific rays, according to their nature; so that, if our eyes were so constructed as to enable us to see these rays, the bodies emitting them would, by the action of these rays alone, appear of different colours, just as they do under the influence of the ordinary luminous rays. According to the experiments of Magnus, rock-salt in particular is not athermochroic, that is to say, diathermanous for all kinds of heat indifferently, but, on the contrary, monothermic, emitting and absorbing only a very limited number of simple rays, just as incandescent sodium emits only a small number of yellow rays, to the exclusion of all other kinds of light.

Magnus made some interesting experiments relating to Thermo-electricity. Becquerel had shown that in a homogeneous circuit, heated at one of its points, electricity is developed by the mere existence of a difference in the quantities of heat propagated on either side of this point. Magnus showed that, in the experiment of the knotted wire,

the production of electricity is not to be attributed to the unequal transmission of heat along the two portions of the wire, but to an alteration in its molecular state. After having demonstrated, as Matteucci had previously done, that no electricity is developed by the contact of two masses of mercury at different temperatures, he showed that a sudden change of diameter, either in a column of mercury or in a perfectly homogeneous wire, produces absolutely no current, but that a development of electricity is always obtained on heating the point of contact of two heterogeneous portions of one and the same wire, one part, for example, being hardened and the other tempered.

Magnus likewise published in the memoirs and monthly reports of the Berlin Academy, and in Poggendorff's Annals, a large number of memoirs relating to various other departments of science; for example, on the Movements of Liquids; the Deviation of Projectiles having a rotatory movement; the Tensions of Mixed Vapours; Electrolysis; the Action of the Keepers of Magnets; and the Diffraction of Light in a Vacuum.

He also contributed greatly to the advancement of science by his labours as a teacher. The lectures which he gave, without interruption for forty years, at the University of Berlin, always commanded numerous and attentive audiences, which he captivated by the clearness and elegance of his language, no less than by the solidity of his instruction. A large number of young physicists have been trained in his physical laboratory to the application of sound scientific methods.

Magnus retained to the close of his life his untiring activity and zeal for the pursuit of science. Towards the end of the year 1869, he experienced the first symptoms of the malady which proved fatal a few months later; but he continued to work, though often suffering severely, till his strength absolutely failed him. He died on the 4th of April, 1870. His death was universally regretted, and his name will ever occupy one of the most distinguished places in the records of science.

Augustus Matthiessen, born January 2, 1831, was the son of a London Merchant. While a child of two or three years old, he had a paralytic seizure, from which he never entirely recovered. As a boy, his fondness for chemical experiment was strongly marked, and his wish, immediately on leaving school, was to devote himself to the study of chemistry; this, however, he was unable to do. While very young, he lost both his parents, and his guardians did not consider themselves justified in sanctioning his devoting himself to physical science, or to his becoming a merchant, believing that the paralytic

affection from which he suffered totally incapacitated him for both pursuits; and believing that the only occupation open to him was farming, they sent him, on leaving school, to serve an apprenticeship to a large farmer in Dorsetshire. Although he was thus frustrated in his desire at once to devote himself to the study of chemistry, his determination was in no wise altered. During the three years which he passed at the farm, he devoted much of the time and money at his disposal to chemical experiments, and immediately on coming of age he quitted the farm and went to Giessen, as being the school where he could best carry out his desire of studying chemistry. Under the direction of Professor Will and Professor Buff, he obtained a thorough knowledge of the elements of chemistry and physics, and during his stay in Giessen he took his degree of Doctor of Philosophy. From Giessen he went to Heidelberg, and under Bunsen's direction at once began the preparation of the metals of the Alkalies and Alkaline Earths and the study of their physical properties. Matthiessen's first paper was published in our Journal for 1855, and is entitled "On the Reduction of the Metals of the Alkaline earths." He was the first to obtain the metals strontium and calcium, decomposing the chlorides by an electric current, and he further clearly showed that both potassium and sodium are incapable of effecting this decomposition. In the laboratory of Professor Kirchoff, he carried on experiments on the physical properties of the metals, and in 1857 published an account of his experiments on the electrical conductivity of sodium, magnesium, calcium, potassium, lithium, and strontium. In the following year he extended this series of researches, estimating the electrical conductivity of many other metals, metalloïds, and some alloys.

In 1857 Matthiessen returned to England, and for a short time worked at the College of Chemistry then under the direction of Dr. Hoffmann; while there he published a short account of the action of Nitrous acid on Aniline. He afterwards had a laboratory at his residence in Torrington Place, and worked there most assiduously for about four years. During this time he published several papers on the specific gravity of different metals and alloys, and also on the electrical conductivity of some alloys and metals, especially gold and copper. In conjunction with Professor G. C. Foster, he published his first paper on the Organic Alkaloïds, establishing the composition of Narcotine, and gaining considerable insight into its rational constitution.

In 1861 he was elected a Fellow of the Royal Society, and in the following year became lecturer on chemistry at St. Mary's Hospital Medical School, a post which he held for six years. He was afterwards chosen lecturer on chemistry, at first in conjunction with Dr. Odling, at St. Bartholomew's Hospital; afterwards, on

Dr. Odling removing to the Royal Institution, Matthiessen became the sole lecturer on chemistry. While holding these chairs of chemistry, his interest in the science never flagged and his indomitable love of work enabled him to accomplish much. His more lately published papers relate entirely to the organic bases, narcotine, morphine, codeine; they all yielded to him most interesting and important results, and he seemed to be on the eve of still more important discoveries. At St. Bartholomew's a new laboratory had been built under his supervision, and he looked forward with pleasure to the increased facilities it would give him for carrying on his scientific researches; but this was not to be; the laboratory had been completed but a few days before his death. Interested in his work to the last, planning new researches, completing old ones, unfailing in his official duties towards his large class of students, and carrying on a large consulting practice, he managed the whole with precision and regularity to the last. Under the strain, which without relaxation, had been put upon his brain for years, it apparently gave way, and on the 6th October last, he died by his own hand.

A man of singular acuteness and wonderful intensity of purpose, what he undertook to do he accomplished and did it well. The personal defects he had to contend against were what few could have overcome, but he was able with complete success to lecture to large audiences, and as a scientific chemist he had reached the foremost rank. In 1869 the Royal Society awarded to him a Royal Medal, and in 1870 he was chosen one of the Examiners of Chemistry at the University of London.

William Allen Miller was born at Ipswich, in Suffolk, on the 17th December, 1817. His early education was conducted by his mother, a lady of remarkable sagacity, good sense, and religious feeling. Those who had the privilege of her friendship, could trace in her son many points of mind and manner in which he closely resembled her. Miller spent one year at Merchant Taylor's School, London, and two years at a school at Ackworth, in Yorkshire, belonging to the Society of Friends. Lectures on elementary chemistry were given at this school, and hence he seems to have imbibed his taste for a science which was to form the business of his life. He also took great pleasure in studying the stars, through a telescope which one of the masters used to exhibit to the pupils. The influence of these early studies may be traced throughout his life, in his devotion to chemistry, and in his application of his knowledge to the chemistry of the stars. His mental training at Ackworth was valuable, and his manner became still more marked by that quiet simplicity which was a characteristic of his mother, as it is also of the members of the Society of Friends.

At the age of fifteen he was apprenticed to his uncle, who was surgeon to the General Hospital at Birmingham. Five years later he became a student in the medical department of King's College, London. Here his chemical knowledge attracted the notice of Professor Daniell, who availed himself of his assistance in the laboratory, during the illness of the appointed assistant. This was the turning point in Miller's career, and gave a decided bias to his studies. In 1839 he gained the Warneford prize for the encouragement of theological studies among medical students. In 1840 he visited Germany, and passed some time in Liebig's laboratory at Giessen. In the same year, he was appointed to the post of demonstrator in the laboratory of King's College. In 1841 he became assistant lecturer to Professor Daniell, and also took his degree of M.D., in the University of London. He likewise aided in various scientific inquiries, and conducted the experiments on the electrolysis of saline compounds which Daniell was then carrying on. Their joint names appear in a paper on this subject published in the Philosophical Transactions for 1844.

In 1845 Miller was elected a Fellow of the Royal Society, and in the same year he was appointed to the Chair of Chemistry in King's College, which had become vacant by the sudden death of Professor Daniell. In the same year he laid before the British Association an account of some experiments on the action of certain gases on the solar spectrum. This paper appeared in the Philosophical Magazine (3rd series, xxvii, 81).

For some years after his appointment, Miller continued to use the work of his predecessor as a text-book for the chemical classes at King's College, supplemented by Fownes's Manual. His own work on chemistry was undertaken after considerable hesitation, lest he should injure the reputation of his master. "You are not aware," he said to the writer of this notice, "how much of Daniell I have in my notes." For some time his idea was to revise Daniell's "Introduction to the Study of Chemical Philosophy," and make such additions as the progress of science required, and to maintain it in its old position as the text-book of the chemical classes. But on looking over the work with this view, he found that so many additions and alterations would be required as greatly to supersede the author's peculiar touches. He therefore decided on producing a new work, and to leave "untouched that of his late master, as the true exponent of his views upon some of those branches of science which his researches had contributed to advance and adorn."

These words are from the preface to the first edition of Miller's "Chemical Physics," dated March, 1855. This volume, as well as the two subsequent ones, on "Inorganic" and "Organic Chemistry," which appeared, the one in 1856, and the other in 1857, were written

from Miller's lecture notes, so that when the books were introduced, the students of King's College, far from having to conform to any new method, seemed to recognise in the new text-books the very lectures they had heard.

The three volumes of Miller's "Elements of Chemistry" passed through several editions in the course of a few years. Being successful, they were reprinted, as a matter of course, in the United States of America; but we are informed that, for the later editions, some arrangement was made with an American publisher, whereby the author and his publisher derived some benefit from the sale of the work in the United States. In these later editions, Miller adopted the new method. His conservative principles led him to resist this change as long as it was possible to do so; but having been, during so many years, accustomed to the old notation, he never took kindly to the new. Indeed, it was part of Miller's character to grasp a new idea with a certain amount of mental slowness; but when once fairly appreciated, it was held tenaciously, and not given up without a severe struggle.

Miller was an excellent chemist, thorough in his work, and thorough in laboratory practice and teaching. His views, without being remarkable for originality, always fairly represented the science of the day, and were expressed with great clearness in simple language.

Miller took a great interest in the progress of Spectrum Analysis, and in 1861 lectured on that subject at one of the evening meetings of the British Association, for the advancement of science, at Manchester. It was expected that this lecture would consist, for the most part, of an account of Kirchoff's researches; but to the surprise of many, a large diagram was exhibited, arranged something like a genealogical tree, containing the names of the various discoverers, and the points discovered up to the date of Kirchoff's researches. The lecture was illustrated by a number of experiments, at that time as remarkable for their novelty as for their brilliancy.

At this meeting he presided over the Chemical Section, and read a short paper on "Photographic Spectra of the Electric Light." The full account of his researches on this subject, based upon a very large number of experiments, was laid before the Royal Society, and is published in the Transactions for 1862, p. 861. These researches seem hardly to have received the attention they deserve.

On the 15th January, 1862, Miller repeated his lecture on Spectrum Analysis before the Pharmaceutical Society of London. This lecture was attended by his friend and neighbour, Mr. Huggins; and, while returning home together, Mr. Huggins proposed that Miller should join him in some experiments on the spectra of the heavenly bodies. The results of this joint inquiry were given to the

Royal Society, and were rewarded by gold medals from the Astronomical Society. Miller also gave a course of four lectures "On the Spectra of the Heavenly Bodies," at the Royal Institution in Albemarle Street, in 1867. He likewise delivered a lecture on the same subject to the working men of Exeter, at the meeting of the British Association in that city in 1869.

During many years, Dr. Miller was one of the Assayers of the Mint and of the Bank of England. He also paid great attention to the subject of Water analysis. It will be remembered by many present that in 1865 he gave us a lecture "On some points in the Analysis of Potable Waters." His latest work was the preparation of a thermometer adapted to deep sea soundings.

We all remember the tone of melancholy that was given to the last meeting of the British Association by the sudden illness of our friend, which soon terminated in his death. Although removed at the early age of 53, he had passed a life which, measured by its results, cannot be called a short one. If we were asked to name, in one word, the most marked feature in Miller's character, we should say it was *sagacity*. Well acquainted with the scientific tendencies of the day, cautious in forming as well as expressing opinions, just in his dealings with others, his advice and assistance were sought by persons in various stations, from a Cabinet Minister down to a humble inventor and patentee. His services were of great value to the Royal Society. He frequently served on the Council, and on various Committees appointed by the Society in its own interests and those of science, if the two can be separated. He became Treasurer of the Royal Society in 1861, and, as such, Vice-President. He was one of the original founders of the Chemical Society, was twice President, and frequently served on the Council Board. He has on several occasions contributed to our Journal, but he was not often heard in debate. Indeed, he had a dislike to impromptu utterances, from a feeling that, in the heat of debate, rash things are often said, and the cause of truth and fair dealing endangered. The caution of his character is here again conspicuous, together with his love of truth. These were based on a deep religious belief, which formed the mainspring of his whole life.

Professor Miller received the degree of LL.D. at the University of Edinburgh; that of D.C.L. at the University of Oxford in June, 1868; and of LL.D. at the University of Cambridge in May, 1869, after giving the Reade lecture. He was buried on the 5th October last, in Norwood Cemetery, by the side of his wife, whom he survived one year.

Dr. James Sheridan Muspratt was born at Dublin on the 8th of March, 1821, and was the son of the well-known founder of extensive

chemical works established near Liverpool. He was a pupil of the late Professor Graham, first at Anderson's University, Glasgow, and afterwards in London; he also studied under Liebig at Giessen, where he took his degree of Doctor of Philosophy. He was the founder of a College of Chemistry at Liverpool, and was well known in the scientific world by a variety of publications relating to Chemistry. Among the works which he edited, that styled "Chemistry, Theoretical, Practical, and Analytical, as applied to Arts and Manufactures," is most widely known. A German translation of this work, with numerous additions, has been edited by Dr. Stohmann. Dr. Muspratt died on the 3rd of April, 1871.

The following is a list of his published papers:—

1847. "On the Composition of the Sulphites;" Phil. Mag. [3], xxx, 414; Chem. Soc. Memoirs, iii, 292.
1848. "On the Action of Nitric Acid on the Sulphocyanides and Bisulphides of Ethyl and Methyl;" Chem. Soc. Qu. J., i, 45.
1849. "On the Selenites;" Chem. Soc. Qu. J., ii, 52.
1849. "On Carbonate of Alumina;" Chem. Soc. Qu. J., ii, 216.
1849. "On the Behaviour of Baryta and Strontia before the Blowpipe;" Ann. Ch. Pharm., lxxii, 118.
1850. "On the Identity of Bisulphethylic with Hyposulphethylic Acid, and of Bisulphimethylic with Hyposulphomethylic Acid;" Chem. Soc. Qu. J., iii, 18.
1850. "On Caryophyllin;" Pharm. J. Trans., x, 343.
1850. "Analysis of a Spring at Orrell, near Wigan;" Pharm. J. Trans., x, 59.
1851. "On the Combination of Arsenious Acid with Albumin, with Remarks on Liebig's Theory;" Chem. Soc. Qu. J., iv, 178.
1851. "Analysis of the principal Mineral Spring at Baden-Baden;" Pharm. J. Trans., xi, 151.
1860. "On Molybdate of Ammonia as a Test for Sulphur;" Chem. News, iii, 204.
1862—1867. "Analyses of the Water of Ben Rhydding, in Yorkshire;" Chem. News, iii, 242; "Of the Mineral Waters of Scarborough;" ibid. vi, 278. Of Harrogate; ibid. ix, 181; xii, 26, 37; xv, 244; and of Llandudno, in North Wales; ibid. xi, 14.

Dr. Muspratt was also associated with Dr. Hofmann in several researches on Aniline and Toluidine (Ann. Ch. Pharm., liii, 222; liv, 1; lvii, 261); and published, in conjunction with Mr. J. Dawson, a paper on Carmufellic Acid (Phil. Mag. [4], ii, 293.)

Karl Weltzien, the son of a Livonian merchant, was born in St. Petersburg, but was removed, at the age of ten, to South Germany, on account of his delicate health. The family settled in Karlsruhe, and in 1831 young Weltzien entered the University of Heidelberg as a student of medicine, taking his degree of Doctor of Medicine in 1835. He was however led to this course of study, rather by the love of natural science, than by a desire to enter upon the practice of Medicine, and, accordingly, he devoted himself especially to the study of Chemistry, which he afterwards pursued further under Mitscherlich's direction, in Berlin. On his return to Karlsruhe, he was made Extraordinary Professor of Chemistry at the Polytechnic Institute, and ten years later, on the re-organisation of the Polytechnic Institute, he was appointed Professor of Chemistry and President of the Chemical School. A new laboratory was at the same time fitted up under his direction. Here he worked happily as teacher and investigator for sixteen years,—training many able students, who made important investigations under his direction; writing seven original works on chemical subjects; and performing a large number of original researches, which were published in Liebig's Annalen. He was always ready to apply his scientific knowledge and skill to the general good, with which view he gave instruction in various technical applications of chemistry, and lectured for many years to the Officers of the Artillery, on those departments of the science which relate especially to their profession. He also gave great attention to the sanitary condition of the town, and analysed a large number of spring and well waters, with the view of obtaining an improved water-supply. This last investigation led him to the discovery of a new method of estimating nitric acid.

In 1868 he resigned his Professorship, in consequence of failing health; and the remainder of his life was a constant struggle with severe suffering, which he bore with great fortitude. He died on the 14th of November, 1870.

The following Papers have been read at the Meetings of the Society, between March 30th, 1870, and March 30th, 1871:—

1. "Analysis of Deep Sea Water:" by John Hunter.
2. "On the Refraction-equivalents of the Aromatic Hydrocarbons and their derivatives:" by J. H. Gladstone.
3. "Note on Bromopicrin:" by Thomas Bolas and C. E. Groves.
4. "On an acid Feed-water from the Coal-field at Stellarton, Nova Scotia, and the results of its use:" by Professor How.
5. "On Tetrabromide of Carbon:" by Thomas Bolas and C. E. Groves.

6. "Chemical Researches on new and rare Cornish Minerals:" by A. H. Church.
7. "On the Combinations of Carbonic Anhydride with Ammonia and Water:" by E. Divers.
8. "On a new Gas-furnace for Chemical Operations at a White Heat:" by Charles Griffin.
9. "On Vapour-densities:" by James T. Brown.
10. "On the Precipitation of Solutions of Ammonium Carbonate, Sodium Carbonate, and Ammonium Carbamate by Calcium Chloride:" by E. Divers.
11. "On the Manipulation of Assays of Gold and Silver:" by Charles Tookey.
12. "On some new Bromine-derivatives of Coumarin:" by W. H. Perkin.
13. "On Organic Matter in Water:" by Charles Heisch.
14. "On the Methods for the determination of Carbon in Steel:" by W. D. Herman.
15. "On Fungi and Fermentation:" by James Bell.
16. "On Acetic and Formic Acid obtained from Human Urine during the Chemical Decomposition of Urochrome:" by J. L. Thudichum.
17. "On the production of the Sulphates of the Alcohol-radicals from the Nitrites by the action of Sulphurous Acid:" by E. T. Chapman.
18. "On the determination of Sulphur in Cast Steel:" by A. H. Elliott.
19. "On the Composition of the Hyposulphites:" by E. A. Letts.
20. "Mineralogical Notices:" by N. Story-Maskelyne and Walter Flight.
21. "Note on the Oxides of Nitrogen:" by E. T. Chapman.
22. "On some Derivatives of Anthracene:" by W. H. Perkin.
23. "On some New Derivatives of Coumarin:" by W. H. Perkin.
24. "On the Formula of Glyoxylic Acid:" by H. Debus.
25. "On the action of Sulphuric Acid on the Natural Alkaloïds:" by Henry E. Armstrong.
26. "On an Alkaloïd from Cinchona Bark, hitherto undescribed:" by David Howard.
27. "On the Origin of Nitrates in Potable Waters:" by Charles Ekin.
28. "On the Development of Fungi in Potable Waters:" by E. Frankland.
29. "On the Effects of Pressure on the Absorption of Gases by Charcoal:" by John Hunter.

30. "On the Solubility of the Phosphates of Bone-ash in Carbonic Water:" by Robert Warington.
31. "On the Distillation and Boiling Point of Glycerin:" by Thomas Bolas.
32. "On the Examination of Glucose-containing Sugars:" by C. H. Gill.

The following Lectures have also been delivered:—

"On Vanadium:" by Dr. Roscoe.
"On the Platinum Ammonias:" by Dr. Odling.
"On the Distillation of Wood:" by Mr. Chapman.

The following Fellows were elected Council and Officers for the ensuing year:—

President.—E. Frankland, D.C.L., F.R.S.

Vice-Presidents who have filled the office of President.—Sir B. C. Brodie, Bart., F.R.S.; Warren De La Rue, D.C.L., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; A. W. Williamson, Ph.D., F.R.S.; Colonel P. Yorke.

Vice-Presidents.—H. Debus, Ph.D., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; H. M. Noad, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; T. Redwood, Ph.D.; J. Stenhouse, LL.D., F.R.S.

Secretaries.—A. Vernon Harcourt, M.A., F.R.S.; W. H. Perkin, F.R.S.

Foreign Secretary.—Hugo Müller, Ph.D., F.R.S.

Treasurer.—F. A. Abel, F.R.S.

Other members of the Council.—E. Atkinson, Ph.D.; H. Bassett; C. L. Bloxam; A. Dupré, Ph.D.; F. Field, F.R.S.; M. Holzmann, Ph.D.; H. McLeod; E. J. Mills, D.Sc.; H. E. Roscoe, Ph.D., F.R.S.; W. J. Russell, Ph.D.; R. Angus Smith, Ph.D., F.R.S.; A. Voelcker, Ph.D., F.R.S.

Donations to the Library, 1870—71.

"Spectrum Analysis:" Second Edition: by H. E. Roscoe: from the Author.

"Die Spectral Analyse;" von H. E. Roscoe; autorisirte deutsche Ausgabe, bearbeitet von C. Schorlemmer: from Dr. Roscoe.

"A Sketch of a Philosophy." Part III. "The Chemistry of Natural Substances:" by J. G. Macvicar: from the Author.

"Le Préparateur photographe:" par T. L. Phipson: from the Author.

"Abridgements of Specifications relating to Aeronautics, 1815—1866:" compiled by W. H. Walenn: from the Compiler.

"The Physical Conditions involved in the Construction of Artillery:" by Robert Mallet: from the Author.

"The Solar Eclipse of August 18th, 1868:" by Warren De la Rue: from the Author.

"On Primary and Technical Education:" by Lyon Playfair: from the Author.

"Field Experiments on Mangolds:" by A. Vöelcker: from the Author.

"A Dictionary of Science:" edited by G. F. Rodwell: from the Author.

"Introduction to the Study of Inorganic Chemistry:" by W. A. Miller: from Charles Tomlinson, Esq.

"The Influence of various Manures on different Species of Plants:" by M. T. Masters and J. H. Gilbert: from the Authors.

"Report of the Committee of the British Association on the Treatment and Utilisation of Sewage:" from the Committee.

"On the Rock-salt Deposit of Stassfurt:" by C. Reinwarth: from the Author.

"Effects of the Drought of 1870 on the Experimental Crops at Rothamsted:" by J. B. Lawes and H. J. Gilbert: from the Authors.

"Catalogue of Transactions, Journals, &c., in the Library of the Royal Society:" from the Royal Society.

"Denkschrift an C. E. H. von Mayer:" von C. A. Zettel: from the Royal Bavarian Academy of Sciences.

"Denkschrift an C. F. von Martius:" von C. Meissner: from the Royal Bavarian Academy of Sciences.

Periodicals:—

"Philosophical Transactions," 1869, Part II, and 1870, Part I and II: from the Royal Society.

"List of Officers and Fellows of the Royal Society for 1870:" from the Royal Society.

"Proceedings of the Royal Institution of Great Britain," Vol. VI., Parts II and III: from the Royal Institution.

"Quarterly Journal of Science," 1870–71: from the Editor.

"Journal of the Photographic Society," from June, 1870, to May, 1871: from the Society.

"Pharmaceutical Journal and Transactions," Third Series, Vol. I: from the Pharmaceutical Society.

"Journal of the Society of Arts," 1870–71: from the Society.

"Chemical News," 1870–71: from the Editor.

"The Chemist and Druggist," 1870–71: from the Editor.

"Memoirs of the Royal Astronomical Society," Vol. XXXVI: from the Society.

"Monthly Notices of the Royal Astronomical Society," 1870–71: from the Society.

"General Index to the first Twenty-nine Volumes of the Monthly Notices of the Royal Astronomical Society:" from the Society.

"Quarterly Journal of the Geological Society," 1870–71: from the Society.

"Nature," Part XXXIII: from the Editor.

"The Chemical Society's Transactions."

"The Food Journal," 1870–71: from the Editor.

"The Milk Journal," Nos. 1—6: from the Editor.

"Year-book of Pharmacy," 1870: from the Editor.

"Journal of the Iron and Steel Institute," Nos. 1 and 2: from the Institute.

"Transactions of the Clifton College Scientific Society," Part I: from the Society.

"Transactions of the Royal Society of Edinburgh," Session 1869–70: from the Society.

"Proceedings of the same," Session, 1869–70: from the Society.

"American Journal of Science and Arts," from July, 1870 to May, 1871: from the Editors.

"Journal of the Franklin Institute," from June, 1870 to May, 1871: from the Institute.

"Annual Reports of the Commissioner of Patents (United States)," 1867, Vols. I—IV: from the Commissioner.

"Smithsonian Contributions to Knowledge," Vol. XVI.

"Smithsonian Miscellaneous Collections," Vols. VII, VIII.

"Smithsonian Report," 1868.

"Annual Report of the Department of Agriculture (United States):" from the Smithsonian Institution.

"Proceedings of the American Philosophical Society," Vol. XI, No. 32: from the Society.

"Proceedings of the Academy of Natural Sciences at Philadelphia," January to December, 1869: from the Academy.

"The American Chemist," 1870–71: from the Editor.

"Archives Néerlandaises," Tome V, Livraisons 1, 2, 3: from the Editor.

"Bulletin de l'Académie Impériale des Sciences de St. Petersbourg:" from the Academy.

"Bulletin de l'Académie Royale de Belgique," 1870: from the Academy.

"Annuaire de l'Académie Royale de Belgique," 1870: from the Academy.

"Bulletin de l'Académie Royale de Médécine de Belgique," 1870: from the Academy.

"Gazzetta Chimica Italiana," 1871, Fascicoli 1, 2, 3: from Prof. Cannizzaro.

"Berichte der deutschen chemischen Gesellschaft zu Berlin," 1870–71: from the Society.

"Abhandlungen der königlich-baeyrischen Akademie der Wissenschaften zu München," Band X. Heft 3: from the Academy.

"Sitzungsberichte derselben," 1870–71: from the Academy.

"Verhandlungen der physico-medicinischen Gesellschaft zu Würzburg," Erster Band, 1868: from the Society.

"Journal für praktische Chemie," 1871: from Prof. Kolbe.

"Nieuwe Verhandelingen van het Bataafsch Genootschap der proefondervindelijke Wijsbegeerte te Rotterdam," 1866: from the Society.

"Oversigt over det Kongelige Danske Viderskabernes Selskabs Forhandlinger, og dets Medlemmers Arbeeten," 1870: from the Royal Danish Academy of Sciences.

"Proceedings of the Russian Chemical Society," 1871, Parts I—VI: from the Society.

Dr. The Treasurer in Account with the Chemical Society from March 25, 1870, to March 25, 1871. Cr.

	£ s. d.	£ s. d.
Balance in hand, March 26th, 1870		953 10 2
Dividends on £3,000 Consols		88 10 0
Mathematical Society, paid for gas and coals at Meetings		1 10 0
Sale of Journals by Publisher		51 5 0
Postage and expenses paid in advance by Members abroad		0 13 0
Sundry Receipts from 25th March, 1870, to 24th March, 1871.		
8 Life Subscriptions	168 0 0	
46 Admission Fees	92 0 0	
7 Subscriptions for 1868	13 0 0	
15 ,, ,, 1869	29 0 0	
83 ,, ,, 1870	155 0 0	
322 ,, ,, 1871	580 0 0	
1 ,, ,, 1872	2 0 0	
		1039 0 0
Subscriptions to Fund for Monthly Report:		
For 1870	212 8 0	
For 1872 to 1875, inclusive	8 0 0	
		220 8 0
Assets. £ s. d.		
Balance at Coutts' 1333 1 3		
Three per Cent. Consols 3000 0 0		
		£2354 16 2

	£ s. d.	£ s. d.
Expenses on Account of Journal.		
Editor's Salary { 9 Months at £95 = £71 5s. ; 3 ,, £150 = £37 10s. }	108 15 0	
Printing Journal, and Provision of Authors' Copies of Papers	229 16 4	
Distributing Journals	47 14 4	
To Editor: Translations and Postage incidental on Editing	3 0 0	
		389 5 8
Preparation of Reports of Meetings		26 12 4
Proceedings of the Royal Society		50 0 0
Expenses on Account of Library.		
Librarian's Salary	25 0 0	
Books and Periodicals—English and Foreign	26 8 10	
Binding of Books and Periodicals	9 2 8	
		60 11 6
Collector's Commission on Subscriptions	51 19 0	
Treasurer's Receipt Stamps	1 12 6	
		53 11 6
Clerical Expenses		8 0 0
Stationery and Postage Stamps		22 9 5
Expenses connected with Faraday Memorial.		
Mr. Wyon, for completing Dies of Medal and supplying Medals		58 13 6
Money Grant for Original Research		10 0 0
House Expenses.		
Provision of Tea, &c., at Meetings	20 3 11	
Gas and Lamps for Meeting Rooms	8 8 0	
Coals	2 4 0	
Expenses attendant on Dr. Roscoe's Lecture	1 5 0	
Salary of House Porter	20 0 0	
Hall Porter—Annual Gratuity	2 2 0	
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PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XX.—*The Preparation and Properties of the Oxide of Triethylphosphine.*

By J. M. Crafts and R. Silva.

Wishing to study the action of different bodies, particularly chlorine and bromine, upon the oxide of triethylphosphine, we have been induced to examine a method of preparation of this substance, given by Carius,* which he proposes to use for obtaining it quickly and in small quantities, in preference to the one originally given by Hofmann, which consists in the oxidation of triethylphosphine. A closer study of the admirable method of Carius has brought out some interesting points not noticed by the author; and this process of preparation, by one of the neatest reactions in organic chemistry, proves so convenient that it seems worthy of attention, particularly as the yield of product, which is larger than can be accounted for by the theory of Carius, suggests some new views regarding the action of phosphorus on the iodide of ethyl.

Carius prepares the oxide of triethylphosphine by the action of iodide of ethyl upon phosphorus in sealed tubes at 160°, and subsequently by the action of alcohol upon the first product. He supposes the reactions to be represented by the equations:—

$$2P + 4EtI = PEt_4I + PI_3.$$
$$PEt_4I + C_2H_6O = PEt_3O + EtI + C_2H_6.$$
$$PI_3 + 3C_2H_6O = P(OH)_3 + 3EtI.$$

The second part of the reaction consists simply in again heating the $PEt_4I + PI_3$ with alcohol in the tubes at 160°. The gas (C_2H_6) which is given off makes it necessary that the tubes should be strong, and that small quantities of material should be used.

Although the above reaction is the only one that a chemist would have considered likely to take place between the iodide of ethyl and phosphorus, it does not correspond with the actual results of experiments, in respect either to the quantity or to the quality of the products.

The product actually obtained is nearly insoluble in water, and is not decomposed, except to a slight extent, even on boiling with water, while the iodide of tetrethyl-phosphonium is soluble in water, and iodide of phosphorus is readily decomposed by that agent. Moreover,

* Ann. der Chem., cxxxvii, 117.

instead of one-half of the phosphorus, we have succeeded in transforming nearly the whole into the oxide of triethylphosphine.

We shall give more fully in another place our experiments upon the crystalline body, which is the immediate product of the action of phosphorus on iodide of ethyl; it is sufficient to state here that it is deeply coloured with iodine, and that it owes its insolubility in water, and its other properties, to an admixture of iodine, which is set free in the first reaction, or rather combines with the bodies PEt_3I_2 and PEt_4I in such a way that it is acted upon by phosphorus with extreme difficulty at a temperature of 180° centigrade. When phosphorus and iodide of ethyl are taken in the proportion given by Carius, there is always a portion of the phosphorus unacted upon, and it is this portion which acts upon the iodine in the second part of the operation so as to give iodide of ethyl and a colourless solution of oxide of triethylphosphine. We conceive that the first reaction, instead of stopping at the phase represented by the equation $2P + 4EtI = PEt_4I + PI_3$, goes further, and that the whole of the phosphorus may be converted into bodies capable of yielding the oxide of triethylphosphine by reactions like the following:—

$$PI_3 + 3EtI = PEt_3I_2 + 4I;$$
$$PI_3 + 3PEt_4I + 2I = 4PEt_3I_2;$$
$$PEt_3I_2 + EtI = PEt_4I + 2I.$$

Of course it is possible to test by direct experiment the feasibility of realizing these and similar reactions; but as we were able to determine by our quantitative results the point which chiefly interested us, namely, the proportion of phosphorus which could be converted into triethylphosphine, we have not made any investigations in that direction.

The most convenient method of preparation of the oxide consists in heating 2 atoms of phosphorus with about 5 molecules of iodide of ethyl (1 part of P and 13 parts of EtI) in sealed tubes for 24 hours at 175°—180°. If the reagents are dry, no gas is formed at this temperature, and at 190°—200° the quantity of gas is small. Large and comparatively thin tubes may be used, since the pressure is not excessive. 300 grms. of iodide of ethyl were used in a single tube, 1 inch in diameter, 2 feet 4 inches long, and $\frac{7}{100}$ of an inch thick in the glass. No tubes were lost by explosions. The phosphorus is at first dissolved and transformed entirely into the amorphous modification, which, being insoluble in iodide of ethyl, is precipitated as a solid cake at the bottom of the tube. The subsequent action is consequently a surface one, and where considerable quantities of material are used, it is useless to heat the tubes in an upright position. They should be placed horizontally, in order to expose as large a surface of phosphorus as possible

to the action of the iodide of ethyl. When the proportions given above or those of Carius, are used, there is always a residue of phosphorus which has not been acted upon. This was found to be the case even when the heating was continued for 60 hours. When a larger proportion of iodide of ethyl is taken, the phosphorus can be entirely dissolved.

The product in the tubes consists of a layer of iodine-coloured crystals, mixed with some liquid, when the iodide of ethyl is in excess, and overlying a cake of red amorphous phosphorus. The crystals are melted and the liquid is poured into a retort, and in order to transform all the iodine into iodide of ethyl, the remaining phosphorus is pulverized and added to the substance in the retort. The whole is boiled with alcohol of 97 p. c. until no more iodide of ethyl is obtained, and the alcoholic solution is colourless.

The crystals dissolve readily in alcohol; their solution has a deep red colour. (The free iodine in the solution can be removed by boiling with zinc-turnings.) The residual product of the treatment with alcohol crystallises as a white solid when the solution is concentrated. It appears to consist of the oxide and the hydrate (PEt_4OH), combined with the acids of phosphorus and a little iodine. This residue is distilled in a copper retort with about 4 parts of solid caustic potash. A small quantity of a gas not absorbable by bromine (C_2H_6), a little phosphoretted hydrogen, and triethylphosphine, are given off during the distillation. Water distils over, and at last the oxide of triethylphosphine, nearly pure. The oxide can be separated from the water by distillation.

The body PEt_3I_2 probably furnishes the oxide by the action of alcohol, and finally of the potassic hydrate, according to the equation:—

$$PEt_3I_2 + 2KOH = PEt_3O + 2KI + H_2O,$$

or, if the action of the alcohol is taken into account—

$$PEt_3I_2 + 2C_2H_6O = PEt_3O + 2EtI + H_2O.$$

In either case no gas should be given off.

The decomposition of the body PEt_4I, as is known by Hofmann's investigation, is attended with the formation of hydride of ethyl:

$$PEt_4I + KOH = PEt_3O + KI + C_2H_6.$$

Therefore, by measuring the quantity of gas given off from a weighed quantity of crystals during an operation, the relative proportions of PEt_3I_2 and PEt_4I can be estimated. The former body was found to be produced in far the larger quantity.

If the distillation in a copper retort is inconvenient, all the oxide can be separated as an oily layer, containing also a certain quantity of

the hydrate (PEt_4OH), by addition of solid caustic potash to the residue after treatment with alcohol; and this layer, distilled in glass, yields the pure oxide, leaving a small residue, consisting mostly of iodide of potassium.

The following are the results of different preparations:—

First. 22·7 grms. of P and 200 grms. of EtI, heated 60 hours at 175°—180°, gave 45·5 grms. of pure PEt_3O. 155 grms. of EtI were regained. Iodine, equivalent to 28·8 grms. of EtI, remained combined with the potash, and 16·2 grms. of EtI were lost. 5·3 grms. of amorphous P remained unacted upon after the treatment with alcohol, so that only 17·4 grms. of P took part in the reaction. According to Carius' equation, this quantity of phosphorus should give 37·6 grms. of oxide of triethylphosphine.

The quantity of P which was dissolved in the alcohol in the form of the acids of phosphorus, was determined from a fraction of the solution, after heating with pure sodic hydrate, as the pyrophosphate of magnesium.

The 17·4 grms. of P, which entered into the reaction, are accounted for as follows:—

		grms.
P dissolved in the alcohol as acids of phosphorus	=	3·8
P obtained in the form of PEt_3O = 10·5 grms.		
P in the form of PEt_3O, lost during the distillation, &c. ..... = 3·1 „		
	=	13·6
		17·4

More than four-fifths of the phosphorus was converted into the oxide of triethylphosphine.

It is to be observed, that a considerable part of the 3·8 grms. merely dissolved during the treatment with alcohol, to combine with the free iodine, and that it did not take part in the first reaction in the tube. When this part is deducted, the yield of oxide of triethylphosphine appears still more favourable.

2nd preparation:

85·3 grms. of P, and 415 grms. EtI were heated 5 hours at 180°.

57· grms. of P remained unacted upon: therefore 28·3 grms. of P entered into the reaction.

89·5 grms. of pure PEt_3O were obtained, and 325 grms. of EtI were regained.

28·3 grms. P, according to Carius' equation, should give 61·1 grms. PEt_3O.

3rd preparation:

47 grms. of P, and 500 grms. EtI were heated 24 hours at 175°.

Only 34 grms. of P took part in the reaction.
106 grms. of pure PEtO were obtained.
34 grms. of P, according to Carius' equation, should give 73·4 grms. PEt_3O.

4th preparation:
53·1 grms. of P and 528 grms. of EtI were heated 24 hours at 180°.
37·6 grms. of P took part in the reaction.
96·5 grms. of pure oxide were obtained.
37·6 grms. of P should give, according to Carius' equation, 81·2 grms. of PEt_3O.

A number of other preparations were made with similar results.

Our equations require twice the amount of product of that of Carius, and the results correspond sufficiently well with the theory, since a loss can scarcely be avoided in operations of this kind, particularly during distillation from a retort containing a large solid residue.

Properties of the Oxide of Triethylphosphine.

There is little to add to the description of the properties of this body, which the well known investigation of Hofmann has made familiar to us.

The boiling point of the pure oxide is 242·8°—243°: no correction.

Its crystallising point is 51·9°. The thermometer remains for a long time stationary at this point, and sinks two or three degrees only as the mass becomes pasty.

The oxide is very hygroscopic, and a quantity of water too minute to be detected by analysis, lowers its boiling and crystallising points considerably.

Since water and the oxide contain nearly the same percentage of hydrogen, the presence of moisture can only be detected by a loss of carbon in the analysis.

The phosphoric acid formed by the combustion of the oxide is apt to enclose traces of carbon, so that the analyses are not absolutely accurate.

I. Oxide of triethylphosphine boiling at 242·8°—243°, and crystallising at 51·9° gave—

Substance = grms. 0·3675; CO_2 = 0·7195; H_2O = 0·3720.

II. The oxide boiling at 242·9°—243°, and crystallising at 51·7°, gave—

Substance = grms. 0·4248; CO_2 = 0·8330; H_2O = 0·4233.

III. The oxide boiling at 242·4°—242·9°, and crystallising at 47·3°, gave—

Substance = grms. 0·2350; CO_2 = 0·4567; H_2O = 0·2420.

IV. The oxide boiling 239·4°—242·4°, and crystallising at 41·4°, gave—

Substance = grms. 0·4645; CO_2 = 0·9105; H_2O = 0·4775.

	I.	II.	III.	IV.	Theory.
C =	53·39	53·48	53·00	53·45	53·73
H =	11·25	11·07	11·43	11·42	11·19

The portion of the oxide which boils at 230°—240°, remains liquid at the ordinary temperature, but still contains very little water.

The oxide, mentioned as pure in the above preparations, boiled at 240°—243°.

Very little of the oxide is carried over with the vapour of water during a distillation, so that its separation from water by that means is easy.

Various unsuccessful attempts were made to obtain triethylphosphine from the oxide: not a trace of that body is produced by the reducing action of zinc upon the oxide in alkaline solution. It is known that the metals, even sodium, do not reduce the oxide, but the sulphide can be reduced by them; it was therefore sought to transform the oxide into the sulphide, but without success. Sulphuretted hydrogen is entirely without action on the oxide. Sulphur, when boiled with it, at first dissolves in small quantity with a beautiful blue colour, which is not permanent; but on heating for a long time, no sulphurous acid is given off, and no sulphide appears to be formed.

The action of chlorine and bromine upon the oxide illustrates its great stability and its power of resisting the action of oxidising agents.

A solution of the oxide in water, saturated with chlorine, retains its green colour for many days in diffused light, and no hydrochloric acid is formed. The dry oxide may be saturated with chlorine at 100°, and no action takes place; if the solution thus obtained is dissolved in a little water, a considerable part of the chlorine is given off as a gas. When the melted oxide is heated in an oil-bath, and dry chlorine is passed through it, an action becomes noticeable at 180°—200°, and hydrochloric acid is given off. The substitution-product thus obtained, is in great part decomposed by distillation.

The oxide dissolves in bromine with a slight rise of temperature, but on evaporation, almost all the bromine goes off, leaving crystals of the oxide. When bromine is added to a strong solution of the oxide in water, the bromine at first dissolves in the solution, but after a con-

siderable quantity has been added, it separates out and carries with it most of the oxide. The oxide can be almost entirely separated from its solution in bromine by washing repeatedly with water. If a mixture of the oxide and bromine is distilled with water, most of the bromine distils with the aqueous vapour. The pure oxide then distils, leaving only a slight residue, consisting of a bromated product.

In order to obtain an action of bromine upon the oxide, the two bodies were heated in a sealed tube with water. The lower layer, consisting of oxide dissolved in bromine, gradually becomes lighter in colour, and diminishes in quantity. In a case where 72 grms. of bromine and 24 grms. of the oxide were used, the action was nearly completed after heating for five hours at 190°.

The product thus obtained was distilled *in vacuo* with only slight decomposition, and portions were analysed, but we found that the hydrobromic acid formed during the reaction, combined with the substitution-products of the oxide in varying proportions, and that, before studying the chlorine and bromine substitution products of the oxide, it was essential to become acquainted with the action of hydrochloric and hydrobromic acids upon that body.

Iodine combines with the oxide in aqueous solution, and removes a great part of it from the solution, to form a liquid solution of the oxide in the iodine. The oxide can be extracted from this solution by treatment with water, but much less readily than from its solution in bromine. Such a solution boiled with water gives off iodine vapours.

In the case of chlorine, no disposition to form a solution in the chlorine, and to separate from aqueous solution, was noticed in regard to the oxide.

Action of Hydrochloric and of Hydrobromic Acids upon the Oxide of Triethylphosphine.

Hofmann, in his admirable investigation, was chiefly occupied by the remarkable class of new bodies which he produced by the action of bromide of ethylene, chloroform, &c., on triethylphosphine, and gives but a short notice of the action of the halogen acids upon the oxide.* He supposes the action to consist, in the case of hydrochloric acid, in the replacement of the oxygen by chlorine in a part of the oxide—

$$PEt_3O + 2HCl = PEt_3Cl_2 + H_2O,$$

and he analysed bodies containing PEt_3O, PEt_3Cl_2, combined with chloride of platinum and iodide of zinc, which were obtained by adding those reagents to an aqueous solution of the immediate products of the action of hydrochloric acid on the oxide.

* Jahresbericht, 1860, 332.

The replacement of oxygen by chlorine, which leads to the formation of the zinc and platinum compounds, must take place only in the presence of those metals in the aqueous solution; no such action is produced by treating the oxide of triethylphosphine alone, or dissolved in water, with the halogen acids.

In the case of hydrochloric acid, the oxide simply dissolves the gas, and the amount which the solution retains varies with the temperature and the tension of the hydrochloric acid. Not a trace of water is formed, and the product does not contain any compound which can be decomposed by zinc or sodium, with formation of triethylphosphine, as would undoubtedly be the case provided it contained the body PEt_3Cl_2. Dry oxide of triethylphosphine saturated with dry hydrochloric acid gas at any temperature above its melting point, loses a portion of the gas when the solution is heated to a higher temperature; it also loses hydrochloric acid when a current of dry air is passed through the solution.

At 180°—190° the product saturated with hydrochloric acid contained 22·8 p. c. of HCl.

In another experiment, the product saturated at 180° contained 24·2 p. c. HCl. This body solidified to a hard crystalline mass at 122°·7; the temperature sinks to 119° while it is still pasty.

These products lose part of their hydrochloric acid on heating in a current of dry air, or on distillation in the air or *in vacuo*. On distilling in the air, they begin to boil at about 250°, but do not show a fixed boiling point.

The last product, heated in a current of dry air up to the point at which liquid was carried over (225°), contained only 15·1 p. c. HCl, and crystallised at 98·5°.

The first product was distilled under a pressure of 3 inches of mercury, and passed entirely at 170°—180°. It began to crystallise at 96·5°, but during the solidification the temperature rose to 96·9°. The same phenomenon of rise of temperature during crystallisation was observed in other products of the action of the halogen acids upon the oxide. This body contained 15·79 p. c. of HCl.

In order to see whether a difference in the point of crystallisation would serve to separate a definite product, a portion was melted and poured off; the remainder however contained 15·95 p. c. HCl.

The analyses in all cases were made by simply precipitating with nitrate of silver in an aqueous solution containing nitric acid.

It seemed probable that if a definite chemical compound were formed, it would have the composition $PEt_3Cl(OH) = PEt_3O + HCl$. The formula of this body requires 21·4 p. c. HCl.

A substance approaching this composition is obtained in beautiful silky crystals, closely resembling anhydrous sulphuric acid, during the

distillation of the bodies described above. The crystals are formed by sublimation, and completely fill the retort, but they are very light, and were never obtained in large quantity. They immediately disappear if the temperature rises too high, or if a trace of moisture is present.

The conditions most favourable to their formation seemed to exist when a current of perfectly dry hydrochloric acid mixed with air was passed very slowly into one of the products already described, while it was heated in an oil-bath to about 100°, or with a very small naked flame. They appear to form when the oxide containing a smaller proportion of hydrochloric acid than 21·4 p. c. is brought in the form of vapour in contact with hydrochloric acid gas diluted with air.

Analysis of two separate preparations gave—

I. Substance = grms. 0·3316; AgCl = 0·2730
II. Substance = grms. 0·6490; AgCl = 0·5040

	I.	II.	Theory.
HCl =	20·94	19·76	21·4

These crystals, when melted, solidify at 127·5°, and the fact that their melting point represents a maximum towards which bodies containing more and less hydrochloric acid converge, seems to point to a definite chemical composition for the crystals. The melting point given is probably too low, since the crystals are extremely sensitive to moisture, and it is impossible to avoid contact with the air in taking them from the retort.

All these bodies containing hydrochloric acid dissolve readily in water, and the solutions, decomposed by caustic potash, yield the pure oxide.

When one of the dry hydrochloric products is heated with zinc-turnings, hydrogen is given off, and the oxide of triethylphosphine distils, while the portion of it which is retained by the chloride of zinc can easily be separated by the addition of caustic potash. No trace of triethylphosphine is formed.

In order to procure data serviceable in the study of the action of bromine upon the oxide of triethylphosphine, the action of a strong (64 p. c.) solution of hydrobromic acid upon that body was tried at 110° in a sealed tube. The resultant product, after the aqueous solution of hydrobromic acid had been separated by distillation in the air, distilled nearly constant at 205°—210° under a pressure of 2 inches of mercury. An analysis gave—

I. Substance = grms. 0·6170; CO_2 = 0·8082; H_2O = 0·4461
II. Substance = grms. 0·6740; AgBr = 0·5096

	I.	II.	Theory, PEt_3O + HBr.
C =	35·72	—	32·09
H =	8·03	—	7·44
Br =	—	32·17	37·21

This product differs widely from the simplest probable compound of PEt_3O and HBr. If we assume that it is only a solution of HBr in PEt_3O and reckon the Br as HBr, a mixture

containing	32·57 p. c. HBr
and ..	67·43 p. c. PEt_3O
	100·00

should contain—

		Found.
C =	36·23	35·72
H =	7·9	8·03

This product was redistilled at 198°—203° under a pressure of $1\frac{1}{2}$ inches of mercury.

An analysis gave—

I. Substance = grms. 0·7325; CO_2 = 0·9720; H_2O = 0·5425

II. Substance = grms. 0·6810; AgBr = 0·5013

	I.	II.	Theory, PEt_3O + HBr.
C....	36·18	—	32·09
H ..	8·23	—	7·44
Br ..	—	31·16	37·21

In another experiment, when the dry oxide was saturated with hydrobromic acid at 150°, we observed that no water was formed. This product began to distil in the air at 260°, and about one half passed over at 270°—300°. A residue was left in the retort at 310°, which began to decompose.

Hydrobromic, like hydrochloric acid, combines with the oxide of triethylphosphine in the same way that these acids combine with water, and it is only under exceptional circumstances that a compound with a simple chemical formula is obtained. The formation of these combinations render the study of the substitution-products of chlorine and bromine more difficult, and such products must be freed from the acids before attempting to purify them.

There are several questions of interest involved in the study of these substitution-products, which lead us to think that they will repay a thorough investigation. In the higher substitution-products it should be determined whether the several atoms of chlorine and bromine are contained in one or in different atoms of ethyl, bearing in mind the curious results of Lieben; possibly also, as in the case of silicic ethide, an atom of ethyl containing many atoms of chlorine or bromine may be removed and replaced by oxygen, giving rise to a new class of acids of phosphorus. It is also to be hoped that such acids may be obtained by the gradual oxidation of the oxide of triethylphosphine by bromine and water at a high temperature.

Some experiments make it appear that the oxide of trimethylphos-

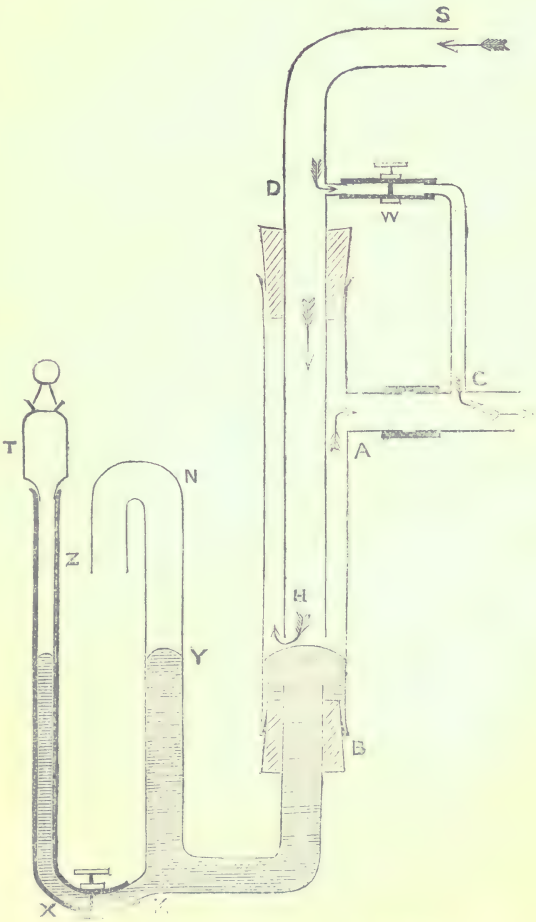
phine may be advantageously prepared by the process already described, and this body may be even better suited than the ethylic compound for the study of its substitution-products.

We are deeply indebted to the kind hospitality of Dr. Williamson for the means of carrying on this research in his laboratory.

XXI.—*An Automatic Thermo-regulator, for use in the preparation of Nitrous Oxide and other Gases.*

By Frank Clowes, B.Sc. Lond.

The accompanying diagram represents in section a modification of the usual air-bath thermo-regulator. It was devised to control the source of heat in the preparation of large quantities of nitrous oxide gas for anæsthetical purposes. It has been in constant use for some time in the laboratory of a distinguished dentist, and has performed its duty perfectly. Its simplicity and efficiency will probably recommend its adoption in laboratories where large quantities of any gas are prepared, whose rate of evolution is dependent upon the amount of heat furnished by a gas-stove or burner.



The broad jacket, AB, has a side tube fused in at A, and is

closed at top and bottom by perforated corks. The upper cork bears a long tube SH, cut square and slightly rounded in the flame at its lower end, which descends nearly to the bottom of the jacket; it has a small tube fused on at D. To ensure the efficient action of the apparatus, the axis of the tube DH must be made to coincide with that of the jacket AB. The lower cork is traversed by a bent tube, NKB, one of whose ends only just passes through the cork; it has a small piece joined on at K, on which fits an india-rubber tube carrying at its upper extremity a small reservoir T, which is suspended by a wire loop to a peg, and can be raised or lowered at will. The side tube at A is joined by india-rubber with a T-piece, C, one branch of which is united by an india-rubber tube, bearing a screw-clamp, with the small side-piece at D, the other branch communicating by gas-tubing with the burner.

When the apparatus is required for use, mercury is poured in at T until it rises sufficiently high in the cylinder to close the lower end of the tube HD; the supply-tube from the gas-pipes is then fitted on at S, the gas passes through SDWC in the direction indicated by the arrows, and is lighted as it issues from the burner; the clamp at W is then tightened until the amount of gas passing to the burner is just sufficient to prevent the flame from being extinguished: the reservoir T is lowered, the clamp at X opened, and the mercury-level in the jacket allowed to fall considerably below the end of the tube SH, so as to give a full supply of gas to the burner through SH. As soon as the gas is being generated in the apparatus at a proper rate, the tube BKN is connected at Z by india-rubber with one of the wash-bottles of the generating-apparatus, whence the gas pressure acts upon the mercury-level at Y; the reservoir T being raised, the clamp at X is carefully opened, and the mercury-level in AB allowed to rise until the gas flame just begins to diminish in size; the clamp is then closed. When the pressure of the generated gas increases, it will depress the level at Y, raising the mercury in AB and diminishing the supply of coal gas, and *vice versâ;* the supply of coal gas to the burner varying inversely as the pressure in the generating apparatus. It was found unnecessary to use a conical float on the mercury, or a slit at H, as the convex surface of the mercury rendered the arrest and renewal of the gas-current sufficiently gradual. The apparatus is drawn pretty nearly to scale; the diameter of the tubes SDH and AC should be about the same as that of the ordinary india-rubber gas-tubing, so as not to impede the free flow of gas to the burner; the diameter of the little side passage DWC may be much less, its object being merely to supply sufficient gas to prevent the total extinction of the flame by a sudden rise of pressure in the generating apparatus; the relative diameters of NYK and AB, must depend upon the rise of mercury-level required in AB. The apparatus was attached to a flat board and suspended upon the wall of the laboratory.

XXII.—*On the Nitration of Chloroform.*

By Edmund J. Mills, D.Sc.

The nitration of chloroform has been attempted, but, according to the ordinary statement*, without success. I find, however, that the task is not altogether impossible of accomplishment.

16 vols. hydric nitrate containing much nitric peroxide are sealed up with 7 vols. chloroform, and heated to 90°—100° for 120 hours. The digesting tubes should lie at an angle of about 30° with the bottom of the bath, as it appears that a more nearly horizontal position involves the destruction of any nitro-compound that may be formed, while an upright position causes the reaction to proceed with excessive slowness. When the digestion is ended, the apparent volume of the chloroform is much greater than before, on account of the liquefied gases, especially nitric peroxide, which it now holds in solution. The tubes are best opened by means of a flame, and allowed to stand about 12 hours; their contents are then poured into water (with which they are washed) and are afterwards dried over calcic chloride and fractionally distilled.

In the course of the distillation, much chloroform comes over first, and is followed by a very small quantity of a liquid, whose nature is not easily mistaken. This second distillate has the extremely pungent and highly characteristic smell of chloropicrin, is nearly colourless, and much heavier than water; a specimen of it boiled at 110·5° in an apparatus in which chloropicrin, prepared from picrate, boiled at 111·6° (corrected temperatures). The determination of chlorine in this specimen furnished the following results:—

Substance.	Argentic chloride.	Chlorine per cent.
0·3287	0·8714	65·54
0·2661	0·7063	65·62

0·6955 grm. chloride from the second estimation yielded 0·5239 grm. silver = 75·33 per cent. (theoretically, 75·28 per cent.), showing that no appreciable quantity of cyanide was present. Another preparation gave the following numbers:—

Substance.	Argentic chloride.	Chlorine per cent.
0·3245	0·8545	65·10

[The theoretical percentage of chlorine in chloropicrin is 64·74. Chloroform contains 89·12 per cent. of chlorine; dinitromethylenic chloride, 40·57 per cent.]

* Watts's Dictionary, i, 920.

0·2371 grm. of the same substance furnished ammonia with aqueous hydric iodide* (of sp. gr. 1·527 at 16°) which was represented by 0·1424 grm. platinum.

	Found.	Chloropicrin.
Percentage of nitrogen.....	8·51	8·52

0·2733 grm. of a fraction boiling at 108°—110·6° (corrected) yielded 0·7334 grm. argentic chloride, corresponding to 6·56 per cent. of chloroform.

0·6049 grm. of the same substance (0·5652 grm. chloropicrin, therefore) corresponded to 0·3334 grm. platinum.

	Found.
Percentage of nitrogen in supposed chloropicrin..	8·35

The chlorine and nitrogen determinations evidently lead to the same result.

The gaseous products of the action of nitrous hydric nitrate upon chloroform, when passed through water, aqueous argentic nitrate, and aqueous baric hydrate successively, gave the usual evidence of free chlorine and carbonic dioxide; while the undecomposed chloroform containing chloropicrin, when poured into water, yielded nitric peroxide copiously with much ebullition.

When chloroform is heated with hydric nitrate under the conditions already detailed, but in the absence of nitric peroxide, it is attacked with much greater difficulty, and the formation of chloropicrin is very doubtful. This observation, taken in connection with the fact that chloroform dissolves nitric peroxide much more readily than hydric nitrate does, raises a fair presumption that that peroxide is the actual agent of nitration.

The homogeneous nitryl of a nitrate, which yields nitric oxide with hydric iodide, is, in chloropicrin, indirectly converted into a different nitryl, which generates ammonia with hydric iodide. On the other hand, alcoholic potash transforms the nitryl of chloropicrin into nitrite-nitryl. Thus, experiment shows that the result of treating chloropicrin with an acid body, is to cause its nitryl to undergo an alkaline change; whereas, in presence of an alkaline substance, the same nitryl is acidified. We have here, then, another instance of what has been demonstrated on previous occasions—that isomerism cannot be interpreted absolutely, but is a question of circumstances.

* Chem. Soc. Journ., xvii, 155.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

On the Ice-calorimeter. By R. Bunsen (Pogg. Ann. cxliii, 616), also by C. Bohn (*ibid.* 618). These notices relate to former suggestions for improvements on the calorimeter of Lavoisier and Laplace.

On the Heat of Combustion of Magnesium and Zinc. By A. Ditte.*

The author proposes to ascertain the relations that exist between the heat developed in the combination of magnesium, cadmium, indium, and zinc with oxygen, and the physical properties of these elements. In the present paper he treats of magnesium and zinc.

By measuring the quantities of heat made sensible, when equivalent weights of magnesium and magnesia are acted upon by similar liquids, and taking the difference, he ascertained the quantity of heat produced when magnesium is oxidized at the expense of hydrogen; and by combining this result with Favre and Silbermann's determination of the heat of combustion of hydrogen, he was enabled to arrive at the desired result. The experiments were conducted in a Favre and Silbermann's mercurial calorimeter. The first consisted in dissolving a known weight of pure magnesium in dilute sulphuric acid, and afterwards dissolving magnesia in the same medium under similar circumstances. By this means he determined the heat of combustion of magnesium with oxygen—as

	Heat units.
For a gram	6,187
For an equivalent.....	74,246

By acting on magnesium with iodic acid, magnesium iodate is formed, and iodine liberated. Making use of this reaction, and of a previous determination of the heat of formation of iodic acid, he re-determined the heat of combustion of this metal, the numbers obtained by this process being in two experiments:—

	Heat units.		
	I.	II.	Mean.
For a gram.....	6092·4	6055·5	6073·9
For an equivalent ..	73,109	72,671	72,890

Treating zinc according to the first method, the author obtained:—

	I.	II.	Mean.
For a gram	1357·0	1358·2	1357·6
For an equivalent ..	44,240	44,276	44,258

S. W.

* Compt. rend., lxxii, 762—766.

On Dissociation from a Thermodynamic Point of View. By J. MOUTIER.*

IN this paper the author points out that when the tension of dissociation is a function of temperature alone, which is generally the case, the formula established by Clausius for vaporization and fusion is directly applicable to dissociation; and consequently that the quantity of heat required to produce a given process of dissociation may be calculated in a manner analogous to that in which the latent heat of fusion or vaporisation can be calculated.

S. W.

On the Explosive Force of Gunpowder and other Detonating Substances. By M. BERTHELOT.†

FOUR data are necessary for expressing explosive force: 1st. The composition of the substance. 2nd. The composition of the products of the explosion. 3rd. The quantity of heat disengaged in the reaction. 4th. The volume of gas produced.

II. The composition of the products of the explosion may be predicted in all cases when the substance contains sufficient oxygen to form stable, completely oxidised compounds. But if the quantity of oxygen be less than this, then the nature of the products varies with the pressure, temperature, work done, &c., and cannot be predicted: in this memoir the simplest expressions, consistent with such facts as are known, are adopted.

III. The quantity of heat disengaged may be experimentally determined, and if the reaction be accurately known, it may also be calculated. The maximum work that can be effected by any explosive material is proportional to the heat evolved.

IV. The volume of gas produced may be experimentally determined, and also, if the reaction be accurately known, it may be calculated.

With these data the pressure produced might easily be calculated if Mariotte's law held good under the conditions of the experiment, and if the specific heat of the gases remained constant; but this latter probably varies with the temperature and pressure, and is entirely unknown, whilst the laws of Mariotte and Gay-Lussac are wholly inapplicable to gases under a pressure of several thousand atmospheres. As, however, it is necessary to use some comparative expression for the pressure produced by different explosive substances, the product of the volume of the gases (reduced) by the quantity of heat in units is employed for that purpose, not as being an exact measure of the true pressure, but as being obtained from two characteristic and experimental elements.

* Compt. rend., lxxii, 759—762. † Moniteur Scient., xiii, 40—57.

To gain a complete notion of the reactions occurring at the explosion, it is necessary to bear in mind the phenomena of dissociation, according to which, the products found after cooling do not exist at the high temperature produced by the explosion, but are replaced by more simple compounds. It follows that the quantity of heat corresponding to the actual reactions is less than the quantity calculated from the products found after cooling.

Under the enormous pressure produced by the explosion, it is probable that the pressure varies much more rapidly with the temperature than is admitted by Mariotte's law, and as the combinations of elements, other conditions being the same, advance in complexity with the pressure, as shown by the author's experiments on the decomposition of acetylene at various pressures, by the electric spark (*Ann. Ch. Phys.* [4] xviii, 196), it will be seen that considerable modifications of the phenomena of dissociation must ensue. This increased influence of pressure may, therefore, fairly be supposed to compensate the decomposing influence of heat.

The phenomena of dissociation doubtless appear at the very commencement of the expansion of the gases; for as the gas expands, it cools, and its elements re-arrange themselves in more complicated compounds; this produces a fresh disengagement of heat, and this action continues during the whole time of expansion. The actual pressure will, therefore, always be higher than the pressure calculated from the quantity of heat disengaged at the moment of maximum temperature, and at first it will be lower than the pressure calculated from the results given by the calorimeter; but as the volume increases, this difference will diminish, and, finally, disappear, the reactions being gradually completed with constant disengagement of heat.

The total quantity of heat, and, consequently, the maximum work done by burning the substance in a known space can be calculated without regard to dissociation, if the final temperature and state of combination of the elements of the products are exactly known.

Heat produced in the Formation of various Nitrogen Compounds.—The memoir contains many theoretical results of reactions of this class, calculated by the author according to methods given (*Compt. rend.* lxxi, 678), and required in comparing the force of different powders, &c., as deduced from the quantities of heat developed by the respective reactions.

The following table contains the numerical results arrived at by the author in the course of this memoir:—

	Quantity of heat evolved by 1 kilo. in units.	Volume of gas formed.	Product of these two numbers, to serve as a term of comparison of the pressures produced.
		mc.	
Sporting powder	644000	0·216	139000
Military powder	622500	0·225	140000
Blasting powder	380000	0·355	135000
Powder with excess of charcoal	429000	0·510	219000
Powder made with sodium nitrate	769000	0·252	194000
Powder made with potassium chlorate	972000	0·318	309000
Chloride of nitrogen	316000	0·370	117000
Nitroglycerin	1282000	0·710	910000
Gun-cotton	700000	0·801	560000
,, with nitre	1018000	0·484	492000
,, with potassium chlorate	1446000	0·484	700000
Potassium picrate	872000	0·585	510000
,, ,, with nitre	957000	0·337	323000
Picrate with potassium chlorate	1405000	0·337	474000

The author then proceeds to examine, with much detail, the behaviour of each of the above-mentioned substances, the following remarks being especially interesting:—

Ordinary Gunpowder.—On comparing the actual products of the explosion with the results of the theoretical equation, $2NO_3K + S + 3C = 3CO_2 + K^2S + N^2$, it appears that the quantity of heat developed in the theoretical reaction is much less than that actually produced: hence it follows that, conformably with a general expression, those products are preferentially produced, in the formation of which the greatest quantity of heat is evolved, the pressure, represented by 139,000, being the same.

Powder containing sodium nitrate was largely employed in excavating the Suez Canal, and with considerable economy: for experiment shows that the substitution of sodium for potassium in any definite salt occasions a nearly constant disengagement of heat. As the alkaline metal exists as a salt, both before and after the explosion, this influence is eliminated if the quantity of heat be calculated for equivalent weights of sodium and potassium salts; but, with equal weights, the volume of gas and the heat, consequently the total work done, will be greater in the case of sodium nitrate, the equivalent of sodium being lower than that of potassium.

Powder containing potassium chlorate. The extreme rapidity with which this powder explodes is due to the enormous quantity of heat evolved by the explosion of the particles first ignited, to the low specific heat of the products, and the comparatively low temperature at which

the chlorate decomposes. As the products are the most simple and stable possible, being binary compounds, the progressive effects of dissociation will be less marked, and the variations of pressure during the expansion of the gases will not be affected by re-combinations of the elements successively produced during cooling. Hence the great detonating quality of this powder. Similar remarks are applicable in a still higher degree to *chloride of nitrogen.*

Nitroglycerin combines the properties of chloride of nitrogen and ordinary gunpowder. This is explicable by considering the effects of dissociation. At the first moment the elements of water and carbon dioxide are separated; but as they recombine during expansion, fresh quantities of heat are evolved, and regulate the fall of the pressure: therefore during expansion nitroglycerin behaves as ordinary gunpowder; but the effects of dissociation are less evident, because the products are more simple, and the initial pressure is higher.

The author then discusses, from the thermodynamic standpoint, the experiments described by Abel (*Compt. rend.* lxix, 105, 121), on the *detonation* of nitroglycerin and gun-cotton. Taking the case of the explosion of nitroglycerin produced by a falling weight, the author calculates that the impact of a weight of several kilos. falling through 0·5m. would raise the temperature of a mass of nitroglycerin but a fraction of a degree, if the heat were distributed equally throughout the mass; but the conversion of motion into heat is too sudden to allow of this distribution; the particles struck may therefore attain the exploding point, 190°; a large quantity of gas is suddenly produced, and this produces a second and more violent shock on the adjacent particles before they have had time to escape from the sphere of action. The force so developed is also converted into heat, and in this way a continuous succession of changes is established throughout the whole mass. The violence of the initial decomposition will increase with the intensity of the first shock, and consequently the pressures produced throughout the entire series of decompositions will rise in equal proportion. Hence one and the same explosive substance will behave in different ways, according to the manner of its inflammation.

These effects are less marked in the case of loose gun-cotton, on account of the large quantity of air interspersed through its bulk. As compressed gun-cotton is less compact than nitroglycerin, it should follow that it is less easily detonated than nitroglycerin; the facts agree with the theory. Nitroglycerin may be detonated by the fall of a weight from a moderate height, by a gun-cotton fuse, or by a mixture of potassium chlorate and fulminate of mercury. Gun-cotton detonates only with a pure fulminate of mercury, and the best results are not obtained unless the fulminate be enclosed in a rather thick case of sheet-tin, and placed in contact with the gun-cotton, conditions

which realise the greatest initial pressure. The quantity of force thus converted depends on the suddenness of the shock, and on the amount of work which it is capable of doing. These elements vary with the detonator, and Abel has found that chloride of nitrogen is not very efficacious, and that iodide of nitrogen, which explodes by the slightest friction, is incapable of exploding gun-cotton. But chloride of nitrogen develops less heat than any other compound here treated of (see table), therefore a larger quantity of it must be employed, and judging by analogies drawn from other iodine substitution-substances, iodide of nitrogen should develop less heat and work than the same weight of chloride of nitrogen. Hence its inactivity in this respect.

Dynamite is found to possess less bursting or breaking power than nitroglycerin; this is explained by the intervention of the inert material, which shares with the nitroglycerin the heat developed by the exploding shock. Thus silica and alumina have nearly the same specific heat as the gaseous products of the explosion of nitroglycerin, the volume being constant; if therefore equal weights of nitroglycerin and either of these substances be fired in a space filled by the mixture, the silica or alumina will absorb half the heat, and proportionally reduce the pressure.

On comparing nitroglycerin with gunpowder, it will be seen that if a given weight of nitre were converted into the exactly equivalent weight of nitroglycerin, it would, in a blast, develop three times as great a pressure as would be produced by the gunpowder made with the same quantity of nitre.

Gun-cotton does not, like nitroglycerin, contain sufficient oxygen for its complete combustion; the products formed on explosion are therefore highly complex. It differs from other explosive substances rather by greater initial pressure than by maximum work; and the empirical results of Piobert [*Traité d'Artillerie, partie théorique*, 496] agree with the calculated result (see table). Theory shows the desirability of causing gun-cotton to explode in the smallest possible space, as practised by Abel in compressing it.

More work may be obtained from gun-cotton by adding to it nitre or potassium chlorate; but as the combustion is then complete, the effects of dissociation during expansion of the products are less evident, and the mixture will have greater bursting power. See also *Nitroglycerin*.

Potassium picrate does not contain sufficient oxygen for its perfect combustion, and is intermediate between gun-cotton and gun-cotton mixed with nitre (see table). Mixed with potassium chlorate it should develop more force than any other solid explosive substance.

F. H. H.

On a New Method of Preparing Supersaturated Saline Solutions. By L. C. De Coppet.*

A so-called supersaturated solution of sodium sulphate may be prepared at ordinary temperatures by simply dissolving the anhydrous salt in cold water. It is necessary to protect the solution from contact with the dust floating in the atmosphere, and to prevent a rise in temperature; the salt must be added in small quantities at a time. If the anhydrous salt has been exposed to the air for any length of time, it must be heated to not less than 40°, and cooled in a closed vessel before being used. Solutions so prepared at 14° contain 35·8 parts of anhydrous sodium sulphate to 100 water. The concentration is therefore nearly three times as great as that of the ordinary solution saturated with the normal crystallised salt, which, at the same temperature, contains 12·4 parts anhydrous salt to 100 water.

Supersaturated solutions of sodium carbonate and of magnesium sulphate may be prepared in the same way.

J. B.

On the Measurement of the Internal Resistance of Voltaic Batteries by the Compensation Method. By W. Beetz.†

The electromotive force of the compensating battery used by the author, is denoted by E, its internal resistance by w, and its external resistance by b. The connecting wire, at two points, between which it possesses the resistance a, is joined by another wire in which a galvanometer, and the battery which is to be compensated, of the electromotive force e, are inserted. The resistances b and a, which can be altered by a sliding arrangement, are so adjusted that the galvanometer is at zero. Then:

$$\frac{E}{e} = \frac{b + w}{a}$$

b and a are now altered to b' and a', so that again compensation takes place. Then—

$$\frac{E}{e} = \frac{b' + w}{a'}$$

from which—

$$w = \frac{a'\,b - a\,b'}{a - a'}$$

when a, a', b and b' are all known.

The author tested his method, first by using thermoelectric elements of exactly the same kind for the compensating, as well as compensated battery, and obtained the following results. The columns E and e

* Chem. News, xxiii, 266.

† Pogg. Ann. cxlii, 573—586.

give the number of elements used, the column $\frac{E}{e}$ gives the ratio of the electromotive forces, as calculated from the known resistances a and b, and the resistance w, as found by experiment. The ratio $\frac{E}{e}$ was determined for each combination of batteries, for as many as four or six different values of a and b; but of each series only one number is given here.

E	e.	$\frac{E}{e}$
II.	I.	2·02
VI.	II.	3·00
X.	II.	5·04
VIII.	I.	8·19
X.	I.	10·20

The author then compared the resistances and electromotive forces of hydroelectric elements, and obtained the following table, in which again only one number of each series for w and $\frac{E}{e}$ is given.

E	e.	w	$\frac{E}{e}$.
1 Grove	1 Daniell	0·275	1·636
1 Grove	1 Lecl.	0·287	1·411
1 Grove	1 Stroehrer	0·292	1·292
3 Lecl.	1 Daniell	4·458	3·440
3 Lecl.	1 Grove	4·489	2·024
4 Stoehrer	1 Grove	0·612	2·341
4 Stoehrer	1 Daniell	0·767	3·992
1 Bunsen	1 Daniell	0·087	1·692
2 Daniell	1 Daniell	1·896	1·974
2 Grove	1 Grove	..	..
$\alpha + \beta$	γ	0·936	0·975
$\beta + \gamma$	α	0·956	1·940
$\gamma + \alpha$	β	1·008	1·950
$\gamma + \alpha$	1 Daniell	1·015	3·313
$\gamma + \alpha$	1 Bunsen	1·056	1·832
3 Meidinger	1 Daniell	11·221	2·797
3 Meidinger	1 Grove	11·428	1·666
1 Grove	1 Meidinger	0·125	1·938

From this it is evident that the method is satisfactory, as the resistance of the same battery remains nearly the same whichever e is taken.

From the numbers obtained in those experiments in which 1 Grove

had been used for compensating, the author calculates the electromotive force of—

1 Grove = 0·916 Bunsen.
= 0·977 Grove.
= 1·295 Stoehrer.
= 1·411 Leclanché.
= 1·647 Daniell.
= 1·938 Meidinger.

or, taking the electromotive force of 1 Daniell as 1:—

1 Bunsen	= 1·799	Daniell.
1 Grove	= 1·684	,,
1 Stoehrer	= 1·272	,,
1 Leclanché	= 1·167	,,
1 Meidinger	= 0·849	,,

R. S.

On the Electromotive Force of Induction in Liquid Conductors. By L. HERMANN.*

RUHMKORFF's apparatus for showing the optical action of magnets was used. The soft iron cylinders of the two bobbins were joined together so as to form a single one. The liquid conductor taken was an india-rubber tube, 179 cm. long, filled with saturated solution of zinc, and closed at both ends with pieces of amalgamated zinc. This was exposed to the inducing action, either alone or together with a metallic conductor, both coiled in six windings of about the same radius, round the soft iron cylinder, and sending the induced current either in the same or in opposite directions, through the galvanometer. The strength of the induced current was measured by the momentary deflections of the needle. The mean of these deflections was—

When the metallic conductor was taken alone	83·3
,, liquid ,, ,, ,, ...	86·4
When both conductors acted simultaneously in the same sense	167·3
When both acted simultaneously, but in the opposite sense	5·8

From these results the author concludes that the electromotive force of the induced current is, *in the widest sense*, independent of the nature of the conductor.

R. S.

* Pogg. Ann., cxlii, 586—590.

On the Electromotive Power of Metallic Sulphides. By WILLIAM SKEY.*

THE author shows that those sulphides which have the power of conducting, are also capable of generating electricity. A mass of iron pyrites and another of galena immersed in sea water and connected by copper wires with a decomposing cell of cupric sulphate, deposited the metal in a coherent form. Other sulphides were examined, and their relative polarity is given in the following list, which is so arranged that each body is positive to all that succeed it:

Ferrous sulphide.
Manganous sulphide (manganese blende).
Zinc sulphide (zinc blende).
Stannic sulphide.
Mercurous sulphide.
Argentic sulphide (artificial).
Lead sulphide (galena).
Cuprous sulphide (copper glance).
Cupric ferro-sulphide (copper pyrites).
Ferric disulphide (cubical pyrites).
Antimonious sulphide (stibnite).
Auric sulphide.
Platinic sulphide.
Ferrous arseno-sulphide (mispickel).
Carbon (graphite) sulphurized.

The author is inclined to believe that much light may be thrown on geological chemistry by such investigations.

S. W.

On the Capability of certain Sulphides to form the Negative Pole of a Galvanic Circuit or Battery. By W. SKEY.†

WHEN a piece of massive galena is placed in voltaic contact with amalgamated zinc, and both are immersed in dilute sulphuric acid, in such a manner as to expose nearly the whole surface of the couple to the action of the acid, a galvanic current is at once established; gas is liberated at the surface of the galena, and the zinc is rapidly dissolved. If three or four such elements be connected together in series, the current produced is capable of decomposing acidulated water.

The galena which forms the negative element in these combinations, may be replaced by other metallic sulphides, such as zinc blende, copper pyrites, protosulphide of iron, &c.: a difficulty, however, arises in establishing a current with iron pyrites, which may be overcome by completely immersing the couple in the acid for a short time; gas is immediately evolved at the point of contact, and the area of evolution rapidly spreads, until the whole surface of the specimen has become active. The gas liberated in a battery of this description is sulphuretted hydrogen, the nascent hydrogen exerting a desulphurising action upon the metallic sulphide, the ultimate effect of which is in some cases

* Chem. News, xxiii, 255. † Chem. News, xxiii, 291.

to completely reduce the mineral to the metallic state. It was further ascertained that these sulphides were able to form among themselves a series of voltaic couples in presence of saline solutions, according as they differed from each other in respect to their affinities for oxygen. Thus, galena and copper pyrites produced a voltaic couple, in which the galena was the negative element, but the functions of the galena were reversed when combined with silver sulphide, this latter mineral being decomposed with less facility.

J. W.

On the Refraction and Dispersion of Light in Silver Iodide, Bromide, and Chloride. By W. WERNICKE.*

THE author has measured the refraction and dispersion of light, in the above-mentioned three silver salts, by two different methods.

First, by examining the light reflected from glass plates covered with a thin layer of silver iodide, bromide, or chloride, with a spectroscope, and noting the position of the dark interference bands seen in the spectrum. The films are obtained by exposing the coating of silver deposited on a glass plate from a suitable silvering solution, to the action of iodine, bromine, or chlorine. By watching the changes of colour taking place during the conversion, the thickness of the film, expressed in wave-lengths of some particular colour, can be calculated, while by means of the weight, extent of surface, and specific gravity of the film, its real thickness becomes known. From these data, and the position of the dark bands in the spectrum of the reflected light, the wave-length of the light in the interior of the film, of that part of the spectrum where the band is seen, is calculated. This wave-length, by comparison with the wave-length in air of the same part of the spectrum, gives the index of refraction of that particular colour.

Secondly, the refraction and dispersion were determined by direct measurements by means of small prisms made by casting the fused salts between plates of parallel glass inclined at the desired angle.

Silver Iodide.

Index of refraction for the line	C.	D.	*b*.	F.	G.
1st method		2·197	2·246	2·267	2·409
2nd „	2·1531	2·1816		2·2787	2·405

The dispersion, $n_G - n_D$, is therefore about 27 times that of water. Silver iodide seems capable of existing in two conditions, one, at temperatures above 138°, of deep yellow colour, perfectly transparent, and giving a short spectrum consisting only of red, yellow, and green;

* Pogg. Ann, cxlii, 560—572.

the other, at temperatures below 138°, of pale yellowish-white colour, less transparent, and producing a spectrum twice as long as the first, though less strongly refracted, and showing all the colours. The author believes that at the higher temperature the silver and iodine are partially dissociated.

Silver Bromide.

Index of refraction for line	C.	D.	F.	G.
1st method		2·261	2·303	2·360
2nd ,, ...	2·2331	2·2533	2·3140	

Silver Chloride.

Index of refraction for line	C.	D.	F.	G.	Hγ.
1st method.....		2·071	2·101	2·135	
2nd ,, ...	2·0462	2·0611	2·0958		2·1309

The dispersion in the two latter salts is, therefore, much less than in the silver iodide, though still considerably greater than in flint glass. But, though the dispersion is greatest in silver iodide, the refracting power of the bromide is greater for most colours. The experiments further confirm a conclusion previously arrived at by the author, viz., that bodies of great dispersive power are transparent only for the less refrangible colours. The temperature during the experiments was 19°; the refractive power diminishes with the rise of temperature. Lastly, the experiments prove that the silver iodide as obtained by precipitation, is identical with that resulting from the direct union of the elements.

A. D.

On the Green Colour of Leaves. By J. J. Müller.*

If a fresh green leaf be held in front of a hand spectroscope which is pointed towards the sun, a continuous spectrum is observed stretching from B to F, and showing no trace of the absorption bands, which are so characteristic of chlorophyl. This spectrum is shown by the fresh leaves of *Cissus antarctica*, *Ficus elastica*, *Convallaria majalis*, and others. On comparing this spectrum with that from white paper, there appeared rather more absorption between D and B than between F and D.

A. P.

* Pogg. Ann., cxlii, 615.

Inorganic Chemistry.

Note on the Specific Gravity of Aqueous Hydriodic Acid. By C. R. A. WRIGHT.*

AQUEOUS hydriodic acid was obtained by the action of hydric sulphide on iodine, and in the weak acid thus prepared excess of iodine was dissolved, and the solution digested at a very gentle heat with phosphorus; finally, the colourless liquid was distilled several times over potassium iodide. Determinations of the specific gravity and percentage of HI were made with specimens of pure acid of different strengths, and from the resulting numbers the following table was calculated by graphical interpolation :—

Percentage of HI.	Sp. gr. at 15°.	Difference for 5 per cent.	Difference for 1 per cent.
0	1·000	0·045	0·0090
5	1·045	0·046	0·0092
10	1·091	0·047	0·0094
15	1·138	0·049	0·0098
20	1·187	0·052	0·0104
25	1·239	0·057	0·0114
30	1·296	0·065	0·0130
35	1·361	0·077	0·0154
40	1·438	0·095	0·0190
45	1·533	0·117	0·0234
50	1·650	—	0·0250
52	1·700		

Contrasting these numbers with those similarly obtained with aqueous hydrobromic acid and those got by Ure with aqueous hydrochloric acid, it appears that hydriodic and hydrobromic acids are alike, in that the increase in specific gravity is not proportionate to the increase in strength, whilst the contrary is the case (or very nearly so) with hydrochloric acid; also that the density of an acid containing a given percentage, x, of HI, is greater than that of one containing the same percentage of HBr, which again is greater than that of acid containing x per cent. of HCl, the density of the hydrobromic acid being always greater than the mean of the corresponding hydriodic and hydrochloric

* Proceedings of the Newcastle Chemical Society, i, 227; Chemical News, June 2nd, 1871.

acids. No numerical relationship is traceable between the atomic weights of these three acids, and the percentages of anhydrous acids contained respectively at the same specific gravity with any strengths of the acids.

C. R. A. W.

On a Compound of Sulphuric Acid with Nitric Acid. By RUDOLF WEBER.*

WEBER has obtained a compound of the empirical formula $4SO_3,N_2O_5,3H_2O$, which he thinks may have the constitution $SO_3N_2O_5 + 3H_2SO_4$. It is obtained by passing the vapour of sulphuric anhydride into very concentrated nitric acid, as free from nitrous fumes as possible. The nitric acid must be well cooled by ice or water, and the anhydride passed in very gradually, with frequent agitation. Crystals of the new compound will be obtained after standing some hours; they are drained on a porous tile over sulphuric acid, and are then colourless and transparent. They are very deliquescent, and contain only traces of nitrous acid; when heated they decompose, with evolution of brown fumes, and a solid body sublimes, which possesses the properties of the compound of sulphuric anhydride with nitrous acid. Weber thinks that the new body is probably analogous in constitution to the well known lead chamber crystals.

A. P.

On the Action of Sulphurous Acid upon certain Metals. By P. SCHWEITZER.†

Zinc and Sulphurous Acid.—A strong solution of sulphurous acid was prepared perfectly free from sulphuric acid, sulphuretted hydrogen, and free sulphur. In this acid, care being taken to exclude atmospheric air, pure zinc was dissolved. No generation of gas could be observed, but the liquid gradually deepened in colour, until it became at last quite brown; it then began slowly to separate sulphur, and after some time regained its original colourless condition.

While the acid was strongly coloured, and before sulphur had begun to separate, part of the liquid was supersaturated with caustic potash, and tested for sulphur with sodium nitroprusside, but no reaction indicative of the presence of a sulphide was obtained. The remainder of the liquid was then allowed to stand, until it had lost its colour, after which it was subjected to the following tests:—A portion of the solution was acidulated with hydrochloric acid, and boiled; sulphur sepa-

* Pogg. Ann. cxlii, 602. † Chem. News, xxiii, 293—295.

rated in large quantity, and sulphurous anhydride was evolved; as this reaction takes place also in the cold, the author considers that it establishes the presence of hyposulphurous acid.

Another portion was diluted, acidified with hydrochloric acid, and tested for sulphuric acid with barium chloride, but no precipitate of barium sulphate was obtained.

A third portion was strongly acidulated with hydrochloric acid, boiled so as to decompose all polysulphur acids, and after filtering off precipitated sulphur, again tested for sulphuric acid; barium chloride now yielded an abundant precipitate of sulphate. As this sulphuric acid was not present in the original solution, it must have been produced by the decomposition of a sulphur acid; the author concludes that this was trithionic acid, interpreting its formation and decomposition in the following manner:—

$$2S_2O_2 + 3SO_2 = 2S_3O_5 + S.$$
$$S_3O_5 = SO_3 + SO_2 + S.$$

The absence of tetra- and pentathionic acids was inferred from the fact, that when the solution was saturated with excess of caustic potash and boiled, no sulphide of potassium was formed.

Respecting the formation of sulphuretted hydrogen when metallic zinc is treated with sulphurous acid in presence of hydrochloric acid, the author does not consider that it is due to a reducing action of the nascent hydrogen upon the sulphurous acid, but rather that it is a necessary consequence of the formation of hyposulphurous acid. When hyposulphurous acid is produced, free sulphur is simultaneously deposited, and this latter, reacting at the moment of its liberation with the escaping hydrogen, produces the sulphuretted hydrogen which is observed in the experiment. It is a fact that sulphuretted hydrogen is only perceived in this reaction after sulphur has begun to separate.

As a more conclusive proof that nascent hydrogen does not reduce sulphurous acid, it was found that by the action of metallic sodium, although a vivid separation of hydrogen took place, no trace of sulphuretted hydrogen could be detected in the escaping gas.

Cadmium and Sulphurous Acid.—Metallic cadmium reacted with sulphurous acid in a manner similar to zinc. The liquid first turned yellow, then darkened, and finally deposited a large amount of cadmium sulphide, this latter, unlike zinc sulphide, being insoluble in weak sulphurous acid. Before any marked precipitation of cadmium sulphide occurred, no sulphuric acid was present in the liquid, but it could be detected in large quantity after the solution had been boiled with addition of hydrochloric acid. The formation of the sulphuric acid is attributed, as before, to the decomposition of trithionic acid, but it is incidentally remarked, that it may possibly result from the reso-

lution of hyposulphurous acid into sulphuric acid and a sulphide, a source which on the whole is much more probable.

Nickel and Sulphurous Acid.—The action of nickel upon sulphurous acid proceeded very slowly. After several hours a darkening and green coloration of the liquid took place, but a long time elapsed before any separation of sulphur resulted. At this stage of the operation, the liquid contained sulphite and hyposulphite of nickel, some free sulphur, but no sulphate or trithionate. After several weeks' standing, a large quantity of nickel sulphide had precipitated, and much sulphuric acid could be found in the solution. From this circumstance, a reaction differing from that of cadmium or zinc is supposed to occur, the nickel hyposulphite, under the influence of, and in contact with, the metal and sulphurous acid, being resolved into sulphuric acid, thereby separating sulphur which combines with the metal.

$$2NiS_2O_3 + SO_2 = 2NiSO_4 + 3S.$$

Aluminium and Magnesium with Sulphurous Acid.—These two metals dissolve readily, the former in cold, the latter in hot sulphurous acid. Neither free sulphur nor sulphuretted hydrogen gas are produced, but upon examining the clear solution, sulphurous, sulphuric, hyposulphurous, and trithionic acids were found, the presence of the latter being inferred from the products of its decomposition. The following equation is supposed to represent the reaction which occurs:

$$4Mg + 8SO_2 = MgSO_4 + MgS_3O_6 + 2MgS_2O_3.$$

J. W.

On a New Method of Formation of Trithionic Acid. By F. Muck.*

The author has found that when manganese sulphide is digested in the cold with ammonium sulphate it assumes a violet grey colour, and that the solution contains manganese and a new sulphur acid, whilst ammonia is set free. If excess of manganese sulphide be present, sulphuretted hydrogen and ammonia are given off, but the solution does not contain ammonium sulphide.

The solution gives the reactions of the polythionic acids, reducing chameleon, and when it is boiled with hydrochloric or sulphuric acids sulphuretted hydrogen is evolved and sulphur precipitated. It exhibits the behaviour of trithionic acid with reagents. A small quantity of mercurous nitrate gives a permanent black precipitate, whilst with an excess it yields a black precipitate, changing to white. With silver nitrate a white precipitate is formed, which rapidly becomes yellow, and finally black. An attempt was made to determine by means of

* Deut. Chem. Ges. Ber., iv, 446—449.

permanganate solution the quantity of trithionic acid formed, and although no good results were obtained, the amount was found to be very small, neither could the trithionate be separated by crystallisation on account of the readiness with which it decomposes.

Ammonium trithionate, ammonia and manganese oxide—the violet-grey substance above mentioned—are formed by the action of ammonium sulphate on manganese sulphide in the following manner:—$2(NH_4)_2SO_4 + MnS = (NH_4)_2S_3O_6 + MnO + H_2O + 2NH_3$. In the presence of excess of manganese sulphide the ammonium trithionate undergoes a further change $(NH_4)_2S_3O_6 + MnS = MnS_3O_6 + (NH_4)_2S$. Finally, no ammonium sulphide is formed by the action of ammonia solution on manganese sulphide. The yellow solution exhibits peculiar reactions, and probably contains a polythionic acid, which the author is engaged in studying.

C. E. G.

On the Sulphazotized Acids. By AD. CLAUS.*

CLAUS has already studied several bodies resulting from the action of sulphurous anhydride on potassium nitrite;† these, however, he believed were not the primary products of the reaction. In order to obtain a more satisfactory result, an alcoholic solution of sulphurous anhydride is added to a solution of neutral potassium nitrite. The product formed is almost insoluble in dilute alcohol, and separates immediately as a white pasty mass. On examination with a microscope, this is found to be a mixture of potassium nitrite and a new body which appears to possess the formula $SO_2.NO_2K$. A purer product is obtained by mixing the solution of potassium nitrite with an equal volume of alcohol, which precipitates some of the salt, and then adding sufficient water to redissolve it. The addition of the alcoholic solution of sulphurous anhydride is continued so long as its smell is rapidly and completely removed. The precipitate formed still contains potassium nitrite, which can be removed by washing with a little cold water.

On keeping, the substance becomes acid, and potassium sulphate is formed. On heating it in the dried state, decomposition with detonation takes place below 100°; on stronger heating, if much nitrite is present, nitrous fumes are evolved, but if the nitrite has been removed, sulphuric acid vapours are given off.

The compound dissolves in 2—3 times its volume of warm water, which on standing deposits crystals of potassium disulphohydroxyazate. On heating to boiling, nitric oxide is evolved; sometimes, however, a single drop of dilute hydrochloric acid is sufficient to start decomposition through the whole solution, during which sulphuric acid is formed.

* Deut. Chem. Ges. Ber., iv, 501—509. † Journ. Chem. Soc. [2], ix, 307.

It can be boiled with water to which potassium hydrate is added, with very little decomposition. On cooling it solidifies to a crystalline mass, which gradually changes to large prismatic crystals. On heating the new body with lead dioxide and water to 40°—45°, an intensely violet solution of potassium trisulphoxyazate, $NO.3SO_3K$, is formed, but on stronger heating in presence of potassium nitrite, violent evolution of gas takes place, and lead sulphate remains. On heating with soda-lime or potassium hydrate, only a part of the nitrogen is evolved as ammonia. More accurate information is deferred to a future paper.

The experiments by Chapman on the formation of sulphates from the nitrous ethers by sulphurous anhydride, seem to confirm Claus's results. The latter thinks it probable that in the first instance a double compound is formed between the nitrite and the sulphurous anhydride, which when heated decomposes into a sulphate and nitric oxide, as in the case of the inorganic compound. Some experiments have been made in this direction. If alcoholic solution of sulphurous anhydride is added to nitrous ether, no reaction takes place; but on the addition of potash heat is evolved, potassium sulphite and nitrite are precipitated, which gradually redissolve, and fine brilliant needles are formed, which are neither nitrite nor sulphite. With ammonia, gases are evolved, and after standing a solid crust of potassium disulphammionate is formed.

A. P.

New Facts about Selenium. By P. Guyot.

Selenium dissolved in carbon bisulphide does not precipitate either acid or neutral salts, except silver nitrate. It precipitates a certain number of metals in alkaline solutions as selenides. With iodine it forms protoiodide of selenium, easily crystallisable.

J. B.

On the Decomposition of Phosphorus Trichloride by Water. By K. Kraut.*

Kraut calls attention to the appearance of phosphorus among the products of the decomposition of phosphorus trichloride by water. From his experiments it appears that when the chloride is added by drops to ice-cold water, with continual stirring, only a trace of phosphorus is obtained; but if the chloride is dropped into boiling water, each addition is attended by a luminous appearance and considerable separation of amorphous phosphorus. The luminous appearance can be avoided by using moderately warm water, when also phosphorus is obtained. When trichloride of phosphorus is distilled with a little

* Ann. Ch. Pharm., clviii, 332—334.

water, or, what is the same thing, with some phosphorous acid, phosphorus separates in reddish-yellow drops, and the residue contains orthophosphoric acid. The reaction would seem to be as follows:—

$$PCl_3 + 4PH_3O_3 = 3PH_3O_4 + 2P + 3HCl.$$

Tribromide of phosphorus behaves with phosphorous acid in a similar way to the trichloride, but the decomposition takes place at a somewhat higher temperature.

W. H. D.

On the Behaviour of Arsenic Acid towards Hydrochloric Acid.
By JOSEPH MAYRHOFER.*

ON distilling hydrochloric acid containing arsenious acid, the whole of the arsenic is found in the distillate; the quantity of arsenic is greater in the earlier portions of the distillate, the later portions are not wholly free from it. From a statement of Rose's, the author hoped to be able to purify some commercial hydrochloric acid by oxidising the arsenic to arsenic acid and distilling. The aqueous hydrochloric acid, of 1·09 to 1·1 sp. gr., was digested with binoxide of manganese, or treated with chlorine, and distilled. No portion of the distillate, however, was perfectly free from arsenic. The author finds that this results from the reducing action of hydrochloric acid on arsenic acid, in consequence of which arsenious chloride and chlorine are produced.

Hydrochloric acid of 1·1 sp. gr. distilled with arsenic acid gave traces—fuming hydrochloric acid and arsenic acid solution when distilled together gave considerable quantities—of arsenic in the distillate.

Arsenic anhydride reacts with hydrochloric acid gas at the ordinary temperature to form chlorine, water, and arsenious chloride. 45 grms. arsenic anhydride required about 100 hours for complete decomposition. The chloride was recognised as arsenious chloride by its boiling point and by analysis.

An attempt was made to form arsenic chloride by passing chlorine through arsenious chloride cooled to $-20°$; the liquid, however, when freed from chlorine by a current of dry air, weighed a few milligrams less than before.

Hydrochloric acid can be freed from arsenic by a method of Bettendorf's,† in which the arsenious acid or chloride is precipitated as metallic arsenic by means of stannous chloride, and the filtered liquid diluted with water to 1·12 sp. gr., is submitted to distillation. This method gives satisfactory results only with the strongest fuming acid.

Hydrochloric acid can also be freed from arsenic by diluting it some-

* Ann. Ch. Pharm. clviii, 326—332. † Zeitschr. f. Chem. [2], v, 492.

what with water, and submitting it to prolonged treatment with sulphuretted hydrogen.

W. H. D.

The Action of Water on Antimonious Chloride. By A. SABANEJEW.*

BY treating antimonious chloride with different proportions of water, compounds corresponding to the formulæ SbClO and $Sb_2O_3.2SbOCl$ were obtained.

SbClO was found to exist in two conditions, amorphous and crystalline. The former was obtained by adding to $SbCl_3$ three times its quantity of water; the crystalline variety by adding to 10 parts of $SbCl_3$, 7 parts of water, and allowing the mixture to remain a few days.

$Sb_2O_3.2SbClO$ was obtained when $SbCl_3$ was treated with from 5—50 parts of water. That produced by the action of cold water crystallised in silky oblique prisms.

A. T.

The Phenomena of Dissociation in Aqueous Solutions of Ferric Chloride. By F. W. KRUKE.†

THE ferric chloride employed was prepared by passing chlorine, in slight excess, through a solution of pure ferrous chloride at a temperature of 50°. The resulting solution was concentrated by evaporation and allowed to crystallise in a cool place. The crystals of ferric chloride thus obtained, when dissolved in water, yielded a solution free from any excess of acid. A standard solution containing exactly 32 per cent. of ferric chloride was then made, and from this, by suitable dilution, all other solutions were prepared.

All solutions of ferric chloride are decomposed on heating, the more readily the more dilute they are. According to the strength of the solutions, the degree of heat to which they are raised, or the length of time during which they are exposed to this heat, the phenomena of dissociation observed may vary. The first effect observed in all solutions, when their temperature is raised, is a greater or lesser degree of darkening, owing to the formation of soluble ferric oxide (Graham's oxide) and free hydrochloric acid. If the temperature be now raised still higher, or continued for some length of time at the same degree, the solution becomes turbid, and deposits, according to concentration or temperature, either difficultly soluble ferric oxide (Péan's), oxychloride, or dense anhydrous ferric oxide. The following table gives

* Zeitschr. f. Chem. [2], vii, 204—207. † J. pr. Chem. [2], iii, 286.

the temperatures at which these various phenomena are observed in solutions of different degrees of concentration:—

Concentration in per cent.	Formation of Graham's Fe_2O_3.		Separation of Péan's Fe_2O_3.	Formation of oxychloride.	Formation of dense Fe_2O_3.
32	100—130°	On cooling, Fe_2Cl_6 is reconstituted.	..	Above 100°	140°
16	100—120°		..	..	120°
8	100—110°		..	..	110°
4	90—100°		..	90°	?
2	87°		..	87°	?
1	83	Remain dissociated on cooling.	100°—130°†	..	..
$\frac{1}{2}$	75		100°—130°	..	..
$\frac{1}{4}$	64		..	..	..
$\frac{1}{8}$	54*		..	..	..
$\frac{1}{16}$	36*		..	..	..

Solutions containing $\frac{1}{16}$ per cent. or less of ferric chloride are decomposed under the influence of light, even at a temperature of 5° or 6° only, though in the dark they keep perfectly at that temperature. Solutions of $\frac{1}{8}$ per cent. and upwards are permanent when exposed to light at ordinary temperature, and a more or less elevated temperature is required for their decomposition.

In the case of gases and vapours, the density furnishes a ready means for estimating quantitatively the amount of dissociation that has taken place, but in the case of solutions the alterations in specific gravity are so slight, and the changes taking place so complicated, that but little help can be derived from this property in estimating the amount of change produced. Nevertheless alterations in the specific gravity, due to dissociation, may be observed in solutions of ferric chloride, as shown in the following table, which gives the specific gravities at various temperatures, of two solutions of ferric chloride, each containing $\frac{1}{8}$ per cent. of the salt. One of the solutions was freshly prepared, the other was old and dissociated.

Temperature.	Freshly prepared and normal.	Old and dissociated.	Temperature.	Freshly made and normal.	Old and dissociated.
0	1·00086	1·00060	60	..	0·98468
10	1·00080	1·00041	70	..	0·97937
20	0·99888	0·99850	80	..	0·97394
30	0·99682	0·99644	90	..	0·96776
40	0·99452	0·99386	100	..	0·96114
50	..	0·98929	..	..	..

* Also when kept for some time at a temperature of 20°.

† Mixed with hydrated ferric oxide.

However, the property possessed by colloïd ferric oxide, to be precipitated from its solutions by the addition of neutral salts of the alkalies, discovered by Prof. Graham, gives us the means of estimating the amount of colloïd oxide present in a solution; and after its removal the amount of unaltered ferric chloride remaining may of course be estimated as usual. Since solutions containing more than 1 per cent. require to be heated to a temperature above 100° before they are decomposed, the author has confined himself to solutions containing 1 and $\frac{1}{2}$ per cent. of ferric chloride respectively. The solutions were heated in an apparatus which permitted a careful regulation of the temperature, and allowed the taking of samples at any desired temperature, at the same time preventing any evaporation. The experimental results are laid down in a series of tables, and may be summed up as follows:—

1. In solutions of ferric chloride the amount of decomposition produced increases with the rise in temperature, but is not proportional to this rise.

2. With a constant temperature the amount of decomposition increases with the time up to a certain maximum. The increase is rapid at first, becomes gradually slower, and reaches the maximum after the lapse of about twelve hours.

The author finally explains the method sometimes employed for separating ferric oxide from manganese, cerium, nickel, and cobalt, carefully neutralising the solution with ammonium or sodium carbonate, and boiling, whereby the ferric oxide is precipitated, while the other metals remain in solution,—as depending on the formation of colloïd ferric oxide, which is then precipitated by the alkali-salt present.

The method proposed by Hofmann and Frankland of purifying sewage by the addition of ferric chloride also illustrates the same phenomena. The very dilute solution of ferric chloride produced is decomposed, as before described, even at ordinary temperature, and the ferric oxide precipitated carries down the other impurities.

A. D.

Contributions to the Knowledge of Indium. By K. J. Bayer.*

Bayer, for the complete and rapid purification of indium from other metals, uses a method based on the fact that soluble indium compounds are completely precipitated by boiling with hydrosodic sulphite, whereas the metals accompanying indium are only partially precipitated by this reagent, and not precipitated at all, if much ammonia salt is present in the solution.

The method of procedure adopted by the author is as follows:—

* Ann. Ch. Pharm., clviii, 372—376.

Freiberg zinc is dissolved in crude hydrochloric acid, with the exception of a small quantity; the solution is allowed to digest in the cold with this undissolved zinc for 24 to 36 hours, whereby all the indium present is precipitated on the zinc; the clear solution of zinc chloride is then poured off, and the metallic deposit removed from the unattacked zinc.

The metallic mud is treated with a few drops of dilute sulphuric acid, to dissolve any basic chloride of zinc, and then washed with hot water until it has no longer an acid reaction. The mixture of metals is then treated with nitric acid; sulphuric acid is added in excess; and the liquid evaporated until all the nitric acid is driven off: by these operations, tin is separated as stannic oxide, and lead as sulphate.

Water is then added, in which the sulphates of indium, zinc, copper, cadmium, iron, and lead dissolve in small quantity. The precipitate is removed by filtration, and well washed, and ammonia in great excess is added to the filtrate, whereby the copper, zinc, and cadmium are dissolved, while all the indium and iron remain behind, accompanied by a little zinc, cadmium, lead, and copper. The well washed precipitate is dissolved in the smallest possible quantity of hydrochloric acid, mixed with bisulphite of soda in excess, and boiled till the smell of sulphurous acid has almost disappeared. The whole of the indium now separates as a white, fine, crystalline powder, perfectly free from copper, zinc, cadmium, and iron. The precipitate is filtered off at once, and washed with hot, air-free water. If much iron is present, the precipitate must be filtered in an atmosphere of carbon dioxide; or better, the iron is completely removed by repeated precipitation with bisulphite of soda.

The precipitate may still contain lead or sodium sulphite; it may be obtained pure by dissolving in aqueous sulphurous acid, filtering from any lead sulphite, and boiling the filtrate.

The crystalline indium compound, dried in vacuo over sulphuric acid, gave on analysis, numbers which the author expresses by the formula $2In_2O_3.3SO_2 + 8H^2O$, adopting 113·4 for the atomic weight of indium, a number supported by Bunsen's recent determination of the specific heat of indium.* The insolubility in water of this sulphite, renders it suitable for the quantitative estimation of indium. From the sulphite, the various indium salts can be prepared, as it dissolves easily in dilute acids, with evolution of sulphurous oxide.

From a solution of the chloride, the indium can be completely precipitated by boiling with potassic nitrite. The precipitate contains neither nitrous acid nor potassium; it consists of the hydrated oxide, $In_2O_3,3H^2O$. W. H. D.

* Page 182 of this volume.

Chemical Changes undergone by some Silver Treasure-trove found at Hildesheim. By A. SCHERTEL.*

THE treasure-trove consisted of some silver vessels which were found in October, 1868. The metal was very much decomposed; every vestige of malleability and toughness being gone. It was very brittle, breaking with a granular fracture. The exterior of the vessels, where they had been in contact with the strata of clay in which they were imbedded, was covered with a crust of silver chloride of varying thickness. This crust, on closer examination, proved to be heterogeneous in its composition. On the exterior was a very thin almost black layer which broke in pieces on attempting to cut it. It gave on analysis 87 per cent. silver, and 12·8 per cent. chlorine. Subchloride of silver contains 85·89 per cent. silver and 14·11 per cent. chlorine.

On this layer was a thicker, paler, and sectile layer of silver chloride: it gave 75·43 per cent. silver and 24·51 per cent. chlorine. Between the silver chloride and the undecomposed metal, was a small quantity of a dark slightly glistening powder, which was gold. One of the fragments, weighed with the adhering silver chloride, 1·665 gram.; without it 1·150 gram; therefore about 25 per cent. of the metal had been converted into chlorine-compounds.

The first two of the following analyses are by the author, the third is from the laboratory at Göttingen:—

	I.	II.	III.
Silver	94·00	98·20	94·78
Gold	2·70	trace	3·18
Copper	3·26	1·56	1·92

The first cause of the change above described is to be sought for in the quantity of copper present (though it is but small). The water filtering through the clay contained a chloride in solution; this chloride acting on the copper converted it into cupric chloride; this in its turn acting on the silver, formed silver chloride and cuprous chloride; the latter was again converted into cupric chloride, and a further quantity of silver was decomposed.

As the superposed clay kept the chloride solution long in contact with the metal, a little copper was enabled to effect the decomposition of a large quantity of silver. The clay too acted as a filter, and thus the thickness of the crust was accounted for. The gold, as the atoms of silver and copper were converted into chloride, settled as a powder on the undecomposed metal.

The author kept a frame, rolled out thin, for six months in a moderately strong solution of salt. At the end of that time it was brittle.

* J. pr. Chem. [2], iii, 319.

0·830 grm. had lost 0·027 grm. A green precipitate had settled on the sides of the vessel. It was dissolved in nitric acid, and the copper determined as sulphide; it gave 0·023 grm. copper.

The alloy had given up 27·7 per cent. of its total contents of copper. The author concludes by drawing attention to one of the methods employed by goldsmiths for colouring golden articles. A mixture of 4 parts of nitre and 2 parts of salt is boiled with a little water until the mass becomes almost thick; 3 parts of hydrochloric acid are then added, and the article to be coloured plunged for a short time into the mixture. If the action be continued too long, or the mixture be too dilute, the metal becomes brittle. This is to be explained by the unequal way in which the gold and copper in the alloy are attacked.

E. T. C.

Mineralogical Chemistry.

Occurrence of Diamonds in Xanthophyllite. By P. v. Jeremejew.*

In the xanthophyllite of the Schischimskian Mountains, near Slatoust, the author has observed diamonds of varying size irregularly distributed through the plates of the mineral. When magnified 30 diameters they are readily recognised, and with 200 diameters their crystalline form is seen to be that of the hexakis-tetrahedron combined with a slightly developed tetrahedron, the faces of the first form being distinctly rounded, those of the latter flat. Most of the crystals are colourless and quite transparent; some have a pale brown tint. They are symmetrically disposed in the matrix, their trigonal intermediate axes being vertical to the foliation of the xanthophyllite. The green plates of this mineral nearest the rounded masses of talcose slate and serpentine, enclose unusually large numbers of them, and they are likewise found in the two rocks themselves.

W. F.

Freieslebenite and Diaphorite. By V. v. Zepharovich.†

Recent observers have variously stated the crystalline system of freieslebenite to be monoclinic, rhombic, or triclinic. The author availed himself of the opportunity of deciding the question which presented itself in the acquisition of a very fine crystal, from Przibram, 2 mm. long, ½ mm. broad, and terminated at one end with 22 exceedingly lustrous faces, together with many other less perfect ones from the same locality. All his determinations accorded in indicating the rhombic system as the true one. The specific gravity of these crystals varying not inconsiderably from that of freieslebenite, the author

* Jahrbuch für Mineralogie, 1871, 275. † Jahrbuch für Mineralogie, 1871, 277.

examined the typical specimens from Freiberg and Hiendelaencina, and found them to agree, in respect to form and density, with the data given in Brooke and Miller's Mineralogy. The Przibram mineral, therefore, is not freieslebenite, as Reuss, from his analytical results, which undoubtedly correspond with the composition of freieslebenite, was led to believe.

The author arrived at the following conclusions:—

1. The mineral hitherto termed freieslebenite consists of two distinct species, the one monoclinic, the other rhombic.

2. The two species have the same composition, but differ in form and density.

3. The substance $Ag_4Pb_3Sb_4S_{11}$, is therefore dimorphous.

4. The rhombic species, which has been termed diaphorite, and has a density = 5·90, is found at Przibram; no freieslebenite accompanies it. At Bräunsdorf, near Freiberg, it is also met with sparsely, and in association with freieslebenite.

5. The monoclinic species, freieslebenite, whose density is 6·35, appears most prominently at Freiberg and Hiendelaencina.

6. The forms of diaphorite and freieslebenite are allied by similar facial inclinations, and they in turn show a relation to the similarly constituted species, stephanite and antimonite. W. F.

On the Cerussite of Kirlibaba in Bukowina. By V. v. ZEPHAROVICH.*

THIS mineral is already known to accompany the galena of this region. Crystals of remarkable beauty have recently been met with, measuring 13 mm. long and 7 mm. broad, and of a yellowish or greyish-white colour. Both as individuals and in groups they are but to a slight degree attached to the quartz or decomposed mica-slate, and consequently exhibit almost perfect development. A prismatic development along the principal axis, and occasionally simultaneously along the brachydiagonal, is generally observed in them. In addition to the three pinacoïds, of which the basal is but slightly developed, there are found the often greatly developed prism ∞P, in a less degree, the brachyprism, $\infty \breve{P}_3$, the brachydomes $\frac{1}{2}\breve{P}\infty$, $\breve{P}\infty$, $2\breve{P}\infty$, $3\breve{P}\infty$, $4\breve{P}\infty$, the pyramid P, and, what is new for cerussite, the brachypyramid $\breve{P}\frac{1}{3}$. The orientation of these forms, often apparently very distorted through dissimilar development of faces, is aided by an almost constant surface character of individual forms. The macropinacoïd always presents a fine vertical striation, sometimes by oscillatory combination with ∞P.

* Jahrbuch für Mineralogie, 1871, 286.

The brachypinacoïd has strongly marked horizontal striation, or decreases gradually by the occasional introduction of the faces of the brachydomes; of the latter, $\breve{P}\infty$ has strong vertical striation. The ratio of the macrodiagonal, brachydiagonal, and principal axis is 1·6396 : 1 : 1·1852. The Kirlibaba crystals often bear considerable resemblance to hexagonal combinations, and some recall the aragonite of Bilin. W. F.

On the Pyro-electric Properties of Topaz. By W. G. HANKEL.*

PYRO-ELECTRICITY is a more common phenomenon in crystals than has hitherto been supposed, and is not confined to hemimorphic minerals. In topaz, and in many other minerals, an extraordinary extension of certain faces may hinder the development of others, and this we are not justified in regarding as hemimorphism. The author, in common with Groth, dissents from Lang's view that topaz is hemimorphic. The pyro-electric phenomena of topaz differ from those observed in hemimorphic crystals of turmaline, calamine, &c., as well in the distribution of the positive and negative electricity, as in the changes brought about in it by differences in crystalline form, imperfect development, or injuries to the crystal. Experiments with many crystals from Schneckenstein in Saxony, Nertschinsk, the Ilmengebirge, Brazil and Asia Minor, led him to the following conclusions:—

1. The pyro-electricity of the crystals is not dependent on hemimorphism, but is probably a property of all crystals, as soon as the remaining physical circumstances allow of its production and accumulation to an amount that can be measured.

2. As in crystals not hemimorphic both ends of one and the same axis are crystallographically similar, they must comport themselves similarly as regards electricity, that is, should exhibit the same polarity, in case they have actually undergone an equal development.

3. The distribution of electricity on crystals not hemimorphic, depends, in addition to their molecular structure, on their external form, and with any changes in the latter, may be modified in a definite manner.

4. As hemimorphism is an exceptional condition in crystallography, so is likewise the appearance of polar axes—axes the ends of which exhibit opposite electricity—an exceptional instance, and is, in fact, dependent on hemimorphic constitution. It appears at present that any change made in the external form of hemimorphic crystals fails to bring about any qualitative variation in the distribution of electricity, and the latter is, therefore, essentially dependent on the dissymmetry of the molecules. W. F.

* Jahrbuch für Mineralogie, 1871, 287.

On Certain Causes of Difference in Crystals of Carbonate of Lime. By H. CREDNER.*

IN an inquiry into the dimorphism of this carbonate, the author sought an answer to the question: has a certain foreign admixture to a mineral solution any influence in determining or modifying the faces of crystals deposited from it? He describes the following experiments:—

1. From a pure and cold solution of bicarbonate of lime, when saturated or moderately dilute, the carbonate separates at ordinary temperatures as calcspar, in the form of the fundamental rhombohedron; when such a solution is more dilute it separates as prismatic aragonite.

2. From a cold solution of bicarbonate, to which silicate of potash has been added, the calcspar that is deposited is remarkably transparent, well defined, and rich in faces. The author had previously noticed that it is from association with apophyllite that certain calcspars of Andreasberg and Lake Superior derive their complex form.

3. When the soda-salt was used in place of silicate of potash, the results were similar.

4. On employing a mixture of the two silicates, the crystals of calcspar presented the same features.

5. From a cold solution of carbonates of lime and strontia in carbonated water, the two being dissolved together, acicular or prismatic aragonite separated, even when the solution was moderately dilute. Bicarbonate of lime, to which bicarbonate of strontia was added or introduced by dialysis, gave acicular and wedge-shaped aragonite, accompanied with crystals of calcspar, the latter increasing in number as the admixture of strontia was reduced. The spectroscope showed the presence of a trace of strontium in the aragonite; in short, such results place it almost beyond doubt that a trifling proportion of strontia is of influence in the formation of aragonite.

6. The addition of a solution of gypsum to cold bicarbonate disposes a portion of the latter to take the form of aragonite.

7. In the presence of a sufficient quantity of lead salt, carbonate of lime crystallises in the form of aragonite. This is seen in nature in the case of tarnovicite. If, however, the amount of lead carbonate present be small, the lime carbonate separates as calcspar, with greater numbers of faces. The general conclusions arrived at by the author are:—I. The addition of certain bodies to a solution of a mineral substance exerts an influence on the form and the number of faces of a crystal deposited from it. II. By the presence of certain bodies in its solution, one and the same mineral substance may receive an impulse to form totally different mineral species. III. Carbonate of lime, which separates from cold pure and not too dilute solutions of its acid

* Jahrbuch für Mineralogie, 1871, 288.

carbonate, as calcspar, is deposited partly in the form of aragonite, on the addition of trifling quantities of carbonate of lead, sulphate of lime, or carbonate of strontia. IV. Differences in temperature and degree of concentration of solution are not the only causes of the dimorphism of carbonate of lime. W. F.

On a New Locality of Meneghinite. By A. FRENZEL.*

THIS mineral species named by Recchi, and hitherto found only at Bottino, in Toscana, has been discovered in the emery bed at Ochsenkozof, near Schwartzenberg in Saxony. It occurs in compact masses, disseminated through the emery, has a metallic lustre, a blackish leaden-grey colour, black brilliant streak, compact to even fracture, hardness = 3, and specific gravity = 6·367. Two analyses gave the numbers:—

	Lead.	Copper.	Antimony.	Sulphur.	Iron.	
I.	61·33	1·38	19·60	17·04	—	99·35
II.....	60·09	1·56	19·11	18·22	0·25	99·23

These results indicate the formula $4PbS,Sb_2S_3$, or that previously assigned to meneghinite. W. F.

On the Composition of Plumbostib and Embrithite from Nertschinsk. By A. FRENZEL.†

THE author gives the results of two analyses (I and II) of the former mineral, the specific gravity of which he finds to be 6·12—6·22, and one of the latter, III, whose specific gravity is 6·32.

	Lead.	Copper.	Antimony.	Sulphur.	
I.	59·64	0·88	19·49	18·95	98·06
II.....	59·44	0·88	21·48	18·14	99·94
III. ..	59·30	0·80	21·47	18·04	99·61

These results correspond with the formula $10PbS.3Sb_2S_3$, and demonstrate the identity of embrithite and plumbostib.

W. F.

On the Occurrence of Amorphous Sulphide of Mercury in the Mineral Kingdom. By G. MOORE.‡

IN Lake County, California, this mineral forms a crust in clefts and hollows on a silicious gangue, associated with cinnabar and iron- and copper-pyrites. It is amorphous, often encrusts iron pyrites, and has

* Jahrbuch für Mineralogie, &c., 1871, iii, 290.
† Jahrbuch für Mineralogie, &c., 1871, iii, 290.
‡ Jahrbuch für Mineralogie, &c., 1871, iii, 291.

many small cavities enclosing crystals of cinnabar. The fracture is conchoïdal to brittle, hardness 3, and specific gravity 7·701—7·748; the colour greyish-black, the streak on porcelain pure black, and, before the blowpipe, it behaves like cinnabar. The mean of several analyses gave these results: sulphur, 13·82; mercury, 85·79; iron, 0·39; and quartz, 0·25. Total 100·25.

W. F.

Two New Pseudomorphs. By A. Reuss.*

In a specimen of bluish-black psilomelane associated with fibrous limonite, from Oberneisen, in Nassau, cavities were observed, one of the largest of which contained pseudomorphic crystals, showing the combination 5R.0R. They are bluish-black, and consist on the outside of a layer of psilomelane of varying thickness; within, however, they are composed in one part of a raspberry-red rhodochrosite, with the cleavage still distinct: in another part only a nucleus of this mineral remains, or has altogether disappeared, and in this case the crust of psilomelane is thicker. The compact psilomelane must have had an origin similar to that of the pseudomorphs, and still consists in some parts of a loose aggregation of rhodochrosite granules, psilomelane occasionally penetrating between and enclosing them. Every stage of the transformation is to be met with. The conversion of rhombohedral carbonates, by absorption of oxygen, and sometimes of water, into higher oxides and their hydrates are well-established facts, that of chalybite into brown iron ore being a familiar example.

The second pseudomorph occurs on a granular quartzite, from Kapnik, through which small crystals of pyrites are disseminated, and whose upper surface is partly covered with crystallised quartz. On this crust are octohedrons, from one-third to one inch in size, and with very cracked drusy surface. The faces of the numberless very small individuals composing them are shown, by the way in which they reflect light, to be in parallel positions. Their surface consists of a blackish-brown blende; below this is a sharply-defined layer of yellowish or reddish-white rhodochrosite, which firmly adheres to the greenish-black nucleus of the crystals, consisting of alabandite, which, though somewhat decomposed, still retains traces of its cleavage and the greenish-black streak. On the pseudomorphs, as well as on the quartz crystals, are small rounded or botryoïdal masses of rhodochrosite. Alabandine is the starting-point of these pseudomorphs. Its octohedrons might at first have become covered with a crust of finely-granular blende, and beneath this the transformation of sulphide of manganese into carbo-

* Jahrbuch für Mineralogie, &c., 1871, 291.

nate may have taken place; the pre-existence of the crust of blende is rendered evident by the presence of small particles of rhodochrosite on the surrounding quartz. W. F.

On the Nephrite (Punamu) of New Zealand. By A. KENNGOTT.*

THE author examined a portion of a block weighing 180 lbs. The fracture was very even, the colour a dull and dirty grass-green, which appeared purer and paler in the thin splinter, and the lustre was inconsiderable. The hardness was 5·0—6·0, and the specific gravity 3·03. Before the blowpipe the thin fragments became white and less lustrous, and fused with some difficulty to a greenish-yellow vesicular slag. As the analyses of this nephrite did not accord with that of other specimens, the author examined a section in the microscope. The slide was sufficiently transparent to allow print to be read through it at a distance of half an inch. With powers from the weakest up to 600 linear, the mass appeared to be made up of one mineral only. It has the appearance of a microcrystalline ground penetrated by numerous fine fibres, and gives one the impression that the material is made up of fine linear crystalloïd bodies irregularly grown together. A section parallel to the nearly even fracture of the nephrite exhibits the tangle of fibres more distinctly than a slide cut at right angles to the fracture. Under crossed and parallel Nichol's prisms, the entire mass presents a beautiful mosaic of blue and yellow which merge into each other and change on rotation. Occasionally small black granules or crystals are seen, the latter having a hexagonal section, sometimes regular, at others with three alternate larger sides, or with an oblong rhomboidal outline. L. R. V. Fellenberg, of Berne, has given an analysis of a specimen of punamu of dark blackish-green colour, which became sea-green when held to the light, and in structure was sinuose and splintery. Its specific gravity is 3·023, and composition: silica, 57·75; alumina, 0·90; iron peroxide, 0·38; iron protoxide, 4·79; manganese protoxide, 0·46; nickel protoxide, 0·22; lime, 44·89; magnesia, 19·86; water, 0·68. Total, 99·93.

Assuming the iron protoxide present as magnetite, the alumina and lime as anorthite, and discarding the water, the oxygen-ratios of these percentages indicate for this mineral the formula $8RO.9SiO_2$, or that formerly assigned to grammatite, with which species it, moreover, approximately accords in the ratio of lime to magnesia, inclusive of the oxides of iron, manganese, and nickel. If, however, the water be considered a constituent, the composition differs still more from that of amphibole. It is probable, then, that this punamu or nephrite is a single species, namely, grammatite.

* Jahrbuch für Mineralogie, &c., 1871, 293.

A comparison of the 25 published analyses of nephrite, mostly from worked specimens and of prehistoric times, has led the author to refer them all to a microcrystalline imperfectly schistose variety of grammatite in the form of a rock of slightly varying composition, the result of admixture. W. F.

On the Occurrence of Baryta in Silicates. By G. C. WITTSTEIN.*

A. MITSCHERLICH found baryta in many felspars, even so much as 2·3 per cent. in some. Subsequently Dr. Ludwig Raab examined 50 silicates, including many felspars, but found no baryta in any.

Wittstein has analysed 50 silicates from the Oberpfalz, and has found that of ten felspars, no fewer than six contained baryta.

	I.	II.	III.	IV.	V.	VI.
Silicic acid	72·006	65·750	65·784	63·825	64·031	69·531
Alumina	10·849	18·220	19·183	19·125	19·323	11·416
Ferric oxide	—	—	—	—	—	3·070
Ferrous oxide	—	0·300	0·134	0·262	0·092	—
Lime	1·932	0·837	0·600	0·974	0·437	2·734
Baryta	2·518	0·500	0·424	0·322	trace	trace
Soda	1·758	3·774	2·836	1·775	2·350	1·142
Potash	10·838	10·325	10·850	13·450	13·650	11·988
	99·900	99·706	99·901	99·733	99·883	90·875

C. H. G.

On the Oil-bearing Limestone of Chicago. By T. STERRY HUNT.†

THE author in this paper brings forward further evidence in support of his original assertion, that the limestone rocks of the Upper Silurian or Lower Devonian is the true source of the petroleum found in the St. Lawrence basin. An examination of the limestone quarries near Chicago, shows that the whole rock seems very uniformly saturated with petroleum, which exudes from the natural joints and fractured surfaces. Specimens of this dolomitic limestone gave on analysis 54·6 p. c. of carbonate of lime. Two portions of 100 and 138 grams respectively were treated with dilute hydrochloric acid. The tarry residue was for the most part soluble in ether. In one case the slight insoluble residue amounted to 0·4 p. c., of which 0·13 was volatile by heat, the remainder being silicious.

The brown ethereal solutions gave on evaporation and subsequent

* Dingl. Polyt. Journ., cc, 336.

† Am. Journ. Sci. [3], i, 420—424.

drying at 100° C. 1·570 and 1·505 p. c. of the weight of the rock taken. This oil was reddish-brown, viscid, and of 0·935 sp. gr. at 16°.

The author shows that this amount is not so trifling as has been assumed, since an area of one mile of this oleiferous dolomite, one foot in thickness, would contain 8,850,069 gallons of 231 cubic inches. But the Chicago limestone-rock has an average thickness of 35 feet: hence four square miles of it contain as much oil as has been raised during the last ten years in Pennsylvania, the total produce from 1860 to 1870 having been twenty-eight millions of gallons. The author, in conclusion, maintains that this explanation of the source of the petroleum in the St. Lawrence basin is the only satisfactory one.

C. G.

On the Geology of the Delta and the Mud-lumps of the Passes of the Mississippi. By Eug. W. Hilgard.*

The mud-lumps, or islets, which occur in the passes of the Mississippi below New Orleans, originate in upheavals of the bottom in the region lying between the extreme point of the mainland and the crest of the bar at the main outlet of the passes. The upheaval varies from an almost secular rate to as much as several feet in 24 hours. They are found in all stages of progress; the islet bearing its first tuft of rushes, the active mud-cone giving out mud accompanied with gas; the extinct and collapsed cone surrounded by its circular wall; and lastly, the shoal—the end of all of them. Various theories have been held as to the cause of these mud-lumps. The author holds, however, with Lyell, that their formation is due to the pressure exerted by newly-formed deposits upon a substratum of yielding mud, accompanied incidentally by evolution of gas. A large portion of the paper is devoted to this question and its bearings on the recent geology of the Mississippi.

The gases given out, together with water and mud, from the active mud-cones, were analysed by the author with the following results:—

	"Knight's Well," New Orleans.	East Crater. Marindin's Lump. Passe à l'Outre.
Carbonic acid	2·97	9·41
Marsh-gas	91·81	86·20
Nitrogen	5·32	4·39
	100·00	100·00

The waters of different springs gave on analysis the following results:—

* Am. Journ. Sci. [3], i, 238—246, 356—368, 425—435.

Analyses of Waters from Mud-lump Springs, Mississippi Passes.

	South-west Pass. I.			North-east Pass. Salt Spring Island. February. II.			North-east Pass. Salt Spring Island. December. III.			Passe à l'Outre. Marindin's Lump. East Crater. IV.			Passe à l'Outre. Marindin's Lump. West Crater. V.		
	a.	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*
Chloride of sodium	2·5374	80·060	81·662	2·7847	81·937	84·117	2·7751	82·809	84·670	} 1·2439	79·094	85·857	{ 1·7544	79·708	84·055
„ potassium ..	0·0280	0·884	0·901	0·0441	1·297	1·332	0·0441	1·316	1·346				{ 0·0166	0·754	0·795
„ calcium	0·0725	2·287	2·388	0·0342	1·006	1·033	0·0638	1·903	1·947	0·0018	0·124	0·124	0·0649	2·947	3·109
„ magnesium..	0·4635	14·224	14·917	0·4475	13·168	13·518	0·3945	11·773	12·037	0·1962	12·475	13·543	0·1259	11·440	12·061
Sulphate of calcium	0·0007	0·022	0·023	..	..	..	..	..	..	0·0069	0·439	0·476	..	..	..
Carbonate of calcium....	0·0011	0·035	..	0·0313	0·921	..	0·0001	0·003	..	0·0695	4·419	..	0·0230	1·045	..
„ magnesium..	0·0446	1·407	..	0·0447	1·315	..	0·0724	2·160	..	0·0392	2·492	..	0·0745	3·385	..
„ iron	0·0158	0·490	..	0·0121	0·356	..	..	..	..	0·0119	0·757	..	0·0128	0·582	..
Silica	0·0007	0·022	..	..	..	..	0·0012	0·036	..	0·0033	0·210	..	0·0030	0·139	..
	3·1643	99·840	99·891	3·3986	100·000	100·000	3·3512	100·000	100·000	1·5727	100·000	100·000	2·2010	0·06100	100·000
Specific gravity	..	1·02388	..	..	1·0244	..	..	..	..	..	1·01190	..	..	1·01689	..

a. Ingredients in 100 ccm. of the water. *b.* Ingredients in 100 parts of solid residue. *c.* Ingredients in 100 parts of solid residue exclusive of carbonates and silica.

TABLE—*continued.*

	Knight's Gas Well. New Orleans. VI.			Gulf Water. 30 miles out. VI.		Sea water. Average composition. VII.	
	a.	*b.*	*c.*	*a.*	*b.*	*a.*	*b.*
Chloride of sodium	0·02310	37·880	56·479	1·6723	76·870	2·700	77·032
„ potassium ..	0·00790	12·950	19·315	0·0357	1·640	0·070	1·997
„ calcium	0·00060	0·980	1·467	..	..	..	..
„ magnesium ..	0·00630	10·330	15·404	0·2310	10·620	..	10·271
						0·360	..
Bromide of magnesium ..	..	..	..	trace.	trace.	0·002	0·058
Sulphate of calcium	0·00300	4·920	7·335	0·1077	4·950	0·140	3·994
				0·1289	5·920	0·230	6·562
Carbonate of calcium....	0·01120	18·360	..	..	..	0·003	0·086
„ magnesium ..	0·00760	12·450	..	..	..	..	..
Silica	0·00130	2·130	..	..	..	..	..
	0·06100	100·000	100·000	2·1756	100·000	3·505	100·000
Specific gravity	..	..	..	1·01630		1·0298	

The general results deducible from the foregoing analyses may be thus stated:—

1. There is a general similarity of composition between the waters of the mud-lump springs, pointing to a common origin.
2. The sodium and magnesium show an approximation to the ratio of these constituents in sea-water.
3. The most obvious differences between the mud-lump springs and ordinary sea-water are—the absence of sulphates, and their partial replacement by chlorides,—the presence of large amounts of earthy carbonates as well as of iron. The amount of potassium salts is largely diminished. Bromides which are present in traces only in the water of the Gulf, seem to be entirely absent.

The character of the materials ejected by the mud-lump springs, as determined by the author's investigations, may be summed up as follows:—

The *gas* is such as is evolved by vegetable matter in its first stages of lignitization.

The *earthy matter* contains both river and marine fossils.

The *mud-lump waters* appear to be sea-water more or less diluted and chemically changed by the influence of decomposing organic matter, and the more active ingredients of the river deposit, viz., carbonates of lime and magnesia, and oxide of iron.

The removal of the sulphuric acid, with the attendant formation of pyrites, owing to the reducing action of the organic matter, is easily understood, but the author is unable to account for the increase of

chlorine, since the analyses show an actual replacement of *sulphate* of magnesium by a corresponding quantity of chloride. The diminution of the potassium salts the author believes to be due to the action of the clay.

The remainder of the paper is devoted to geological considerations.

C. G.

Analysis of a Cement Stone. By E. REICHARDT.*

THE stone was found in the neighbourhood of Jena, and is largely employed for the manufacture of cement. It was of a dark-grey colour, possessed a clayey odour, and showed isolated remnants of petrified fish-teeth, and here and there traces of iron pyrites.

The finely powdered material was evaporated twice with excess of concentrated hydrochloric acid; and the insoluble portion, separated by filtration, was fused with barium carbonate, after the removal of the soluble silica by means of solution of sodium carbonate. Both solutions were analysed as usual. The hydrochloric acid solution gave, in 100 parts of the limestone, CaO, 28·05; MgO, 12·96; Fe_2O_3, 3·83; FeO, 4·17; MnO, ·22; Na_2O, ·40; K_2O, ·35; soluble SiO_2, 2·96; CO_2, 36·00; SO_3, ·22. Total 89·16, to which must be added ·66 p. c. of water given off at 120° C., and 10·18 p. c. of residue insoluble in acid.

From these numbers it follows that 35·93 p. c., or nearly the whole of the carbonic anhydride was combined with the lime and magnesia. The percentage found by loss amounted to 36·06, and by means of barium hydrate to 35·91 p. c.; ferric, ferrous, and manganous oxide and the alkalies were partly combined with silica, partly in the free state. The composition of the soluble portion of the stone may be expressed as follows:—

CO_3Ca.	CO_3Mg.	SO_4Ca.	Fe_2O_3.	FeO.	MnO.	Na_2O.	K_2O.	SiO_2.†	H_2O.	
49·84	26·96	0·36	3·83	4·17	0·22	0·40	0·35	2·96	0·66	= 89·75

The residue, insoluble in hydrochloric acid, after being freed from soluble silica by digestion with sodium carbonate, amounted to 10·28 p.c., and gave, for every 100 parts of the limestone, CaO ·76, MgO ·14, Fe_2O_3 ·60, Al_2O_3 1·60, K_2O ·13, Na_2O ·19, SiO_2 3·78; sand 3·26; or,

* Dingl. Polyt. Journ. cc, 219. † Soluble.

Potassic silicate.	Sodic silicate.	Calcic silicate.	Magnesic silicate.	Ferric silicate.	Aluminic silicate.	Sand.	
0·26	0·47	2·01	0·46	0·95	3·04	3·26	= 10·45

The oxygen ratio in the metallic oxides and in the silica, viz.:

R_2O.	R_2O_3.	SiO_2.
1	2·7	3·8

leads to the formula $R_2O.SiO_2 + R_2O_3.SiO_2$, *i.e.*, the formula of zeolite, natrolite, or labradorite.

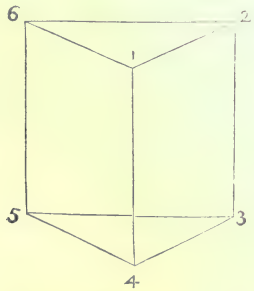
The dolomitic constituents are closely expressed by the formula:— $2MgCO_3.3CaCO_3$. The quantity of iron pyrites was extremely small, 0·1 p. c. of sulphur only being present, = ·175 p. c. of FeS_2. The stone was free from phosphoric acid and chlorine.

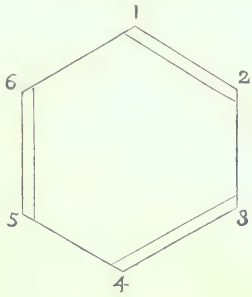
W. V.

Organic Chemistry.

Determination of the Relative Positions of the Substituted Radicals in Aromatic Compounds. By C. Graebe.*

According to Huebner,† the constitution of the bi-substitution products of benzene can be as well explained by the prismatic formula of benzene given below, as by using Kekulé's formula, which represents the carbon atoms in benzene as joined together in a ring, and linked together by one and by two combining units alternately.‡





* Deut. Chem. Ges. Ber., iv, 501—504. † Ann. Ch. Pharm., clviii, 33.

‡ The latter is the only formula of benzene yet proposed which affords a satisfactory explanation of the formation of the additive products, such as $C_6H_6Cl_6$.

But such is not the case; Huebner's own researches have confirmed the author's views on the constitution of the three phthalic acids*, the position of the carboxyls being in phthalic acid 1 : 2, in isophthalic acid 1 : 3, and in terephthalic acid 1 : 4. If we adopt Kekulé's formula we can easily explain why, of these three acids, only phthalic acid forms an anhydride, as it is the only one in which the carboxyls are close together; but in using the prismatic formula, we have not only to assume that the contiguous positions 1 : 2 and 1 : 4 are different, but there is, further, the great difficulty of finding a reason why terephthalic acid does not yield an anhydride as readily as phthalic acid. The fact that, of the three dioxybenzenes, only hydroquinone forms a quinone, likewise speaks in favour of the ring formula.

C. S.

Investigations on Isomerism in the Benzene-Series. XIV.—On the Determination of the Chemical Position in some Toluene Derivatives. By F. Beilstein, and A. Kuhlberg.†

In a former communication‡ the authors had shown that the nitro-groups in dinitrotoluene occupy, respectively, the *para*- and *meta*-positions. Also, that, on nitration of the acetyl-derivative of ordinary, solid (para-) toluidine, the substituted hydrogen occupied the *ortho*-position. It became, then, interesting to ascertain the behaviour of the isomeric toluidines when similarly treated.

I. *Derivatives from Dinitrotoluene.*

Parachloro-metanitrotoluene.—$C_6H_3(Cl)_p(NO_2)_mCH_3$. By partial reduction of dinitrotoluene with ammonium sulphide the nitro-group in the *para*-position is affected§; consequently, on replacement of the amido-group by chlorine, para-chloro-metanitrotoluene necessarily results. This body was prepared by distilling an intimate mixture of the platino-chloride of the diazo-compound obtained from β-nitrotoluidine with 10—12 times its weight of ignited soda, or fine sand.

$$(C_7H_6(NO_2)N_2.Cl)_2.PtCl_4 = 2C_7H_6(NO_2)Cl + N_4 + Cl_4 + Pt.$$

It crystallises in long, glistening, yellowish needles, which are insoluble in water, difficultly soluble in cold, but readily soluble in boiling alcohol, and melt at 38°. It is easily volatilised in a current of steam, and is unaffected by boiling with a mixture of potassium dichromate and sulphuric acid. On reduction with tin and hydrochloric acid, parachloro-metatoluidine hydrochloride, $C_7H_6(NH_2)Cl.HCl$ + aq. is obtained. The nitrate of this body forms long, broad, anhydrous

* Ann. Chem. Pharm., cxlix, 26.
† Ann. Ch. Pharm., clviii, 335—353.
‡ Ibid., clv, 13.
§ Ibid.

needles. The free base is solid, but melts at a comparatively low temperature.

On Paraiodo-metanitrotoluene and Derivatives. By A. HEYNEMANN. —1. *Paraiodo-metanitrotoluene*, $C_6H_3I_p(NO_2)_m.CH_3$, was prepared, according to Griess's directions, by the action of concentrated hydriodic acid on diazonitrotoluene sulphate. It is obtained from alcohol in beautiful, slightly yellowish crystals, which are very soluble in ether and carbon bisulphide, and melt at 60·5°—61°. It is not possible, by the action of chlorine, to replace the iodine by chlorine; further substitution of chlorine takes place.

2. *Paraiodo-metatoluidine*, $C_6H_3I_p(NH_2)_m.CH_3$, was obtained from the former by reduction with tin and hydrochloric acid, &c. It melts at 48°—49°, is very soluble in alcohol, ether, and carbon bisulphide, and crystallises from dilute alcohol, on slow evaporation, in colourless, needle-like crystals. The nitrate separates from a hot aqueous solution, on cooling, in scales having a nacreous lustre. If the solution containing an excess of acid be warmed too long, it becomes of a red colour. 1000 parts of water, at 16°, dissolve 9·5 parts of salt.

It follows, from the constitution of the above base, that *paraiodotoluene*, a body already described by Körner,* must be obtained from it on substituting hydrogen for the amido-group. Unfortunately, this reaction does not admit of realisation. Paraiodo-metatoluidine nitrate can only be converted into the diazo-compound with very great difficulty, and the latter is so unstable as to be decomposed by water, even in the cold. Thus, by the action of nitrous acid, a body was obtained, crystallising from hot water in fine, yellow needles, melting at 165°, which, from the analysis, seems to be *dinitroiodocresol*, $C_6HI(NO_2)_2(OH).CH_3$. It is soluble in soda, and is reprecipitated by hydrochloric acid. This nitro-body is more readily obtained on treating the product of the action of nitrous acid with warm water.

3. *Parabromo-metanitrotoluene*, $C_6H_3Br_p(NO_2)_m.CH_3$, was prepared by decomposition of the perbromide, $C_7H_6(NO_2)N_2Br.Br_2$, of the diazo-derivative of β-nitrotoluidine with alcohol. It crystallises from dilute alcohol in fine, yellowish needles; on slow evaporation in short, thick prisms. Melting point 45°.

4. *Parabromo-metatoluidine*, $C_6H_3Br_p(NH_2)_m.CH_3$, obtained by reduction of the above, melts at 36°. Its nitrate is difficultly soluble in water; 1,000 parts at 17° dissolve 9 parts of the salt.

II. *Derivatives of Paratoluidine.*

1. *Dinitro-acettoluide*, $C_6H_2(NO_2)_2.NH(C_2H_3O).CH_3$, is obtained by the action of nitric acid of 49° Beaumé on para-acetotoluide. It forms

* Zeit. f. Chemie, 1868, 327.

long, pale-yellow needles, much more soluble in hot than in cold alcohol. Melting point 190·5°.

2. *Dinitroparatoluidine*, $C_7H_5(NH_2)_p(NO_2)_2$, is readily prepared from the above by heating with an equivalent quantity of potassium hydrate in alcoholic solution. Yellow needles, difficultly soluble even in hot alcohol; more soluble in benzene; melting point 166°. It is but slowly reduced by tin and hydrochloric acid, and it would seem that toluylenediamine, and not a triamine base, is formed.

3. *Orthonitro-parabromotoluene*, $C_6H_3(NO_2)_oBr_p.CH_3$, was obtained by the action of alcohol on the perbromide of the diazo-derivative of nitroparatoluidine. Slender light-yellow needles, melting at 33°—34°.

4. *Orthonitro-paraiodotoluene*, $C_6H_3(NO_2)_oI_pCH_3$, obtained by the action of hydriodic acid on the sulphate of the diazo-derivative from nitroparatoluidine, forms flat, yellow needles, easily soluble in hot alcohol, extremely soluble in carbon bisulphide. Melting point 55°—56°.

III. *Derivatives of Metatoluidine.*

1. *Orthonitro-metaacettoluide*, $C_6H_3(NO)_{2o}N_mH(C_2H_3O).CH_3$, is obtained by the action of nitric acid of 45° B. on pure metaacettoluid. Crystallises from boiling water, in which it is very difficultly soluble, in microscopic needles, which melt at 196°—197°.

2. *Orthonitro-metatoluidine*, $C_6H_3(NO_2)_o(NH_2)_m.CH_3$, is obtained from the above either by the action of sulphuric acid or of potassium hydrate. It is very difficultly soluble in water, from which it separates in small lemon-yellow needles. The free base crystallises out from a hot dilute nitric acid solution, so that its basic properties are extremely weak. Melting point 127°—128°. By the action of nitrous acid and alcohol it is converted into *orthonitrotoluene*. The circumstance that an *ortho*-derivative is formed by the substitution of hydrogen in metatoluidine is of considerable practical importance. Crude toluidine is a mixture of para- and meta-toluidine; but since identical hydrogen-atoms in each are replaced, it is not necessary, in preparing the ortho-derivatives, first to carry out the troublesome separation of the two modifications of toluidine.

3. *Meta-iodotoluene*, $C_6H_4I_m.CH_3$, is obtained by the action of hydriodic acid on the diazo-derivative from metatoluidine nitrate. A colourless liquid, which boils constantly, without decomposition, at 204°. It cannot be converted, by oxidation, into an acid, but is burnt to water and carbonic anhydride.

4. *Nitro-metaiodotoluene*, $C_6H_3(NO_2)I_m.CH_3$, prepared by the action of fuming nitric acid on meta-iodotoluene. Microscopic needles, moderately soluble in alcohol. Melting point 103°—104°.

IV. *Derivatives of Orthotoluidine.*

1. *Metanitro-orthoacettoluide*, $C_7H_6(NO_2)_m.NH(C_2H_3O)$, was prepared from orthoacettoluide in the same manner as the analogous meta-compound. It crystallises from alcohol in small rhombic prisms from water, in which it is very difficultly soluble, in small needles, or short thick prisms. Melts at 101°—102°.

2. *Metanitro-orthotoluidine*, $C_7H_6(NO_2)_m.(NH_2)_o$. From the above by decomposition with potassium hydrate. Long, slender, saffron-yellow needles, difficultly soluble in boiling water; soluble in acids, and re-precipitated by ammonia. Melting point 133°—134°. In order to determine the position of the nitro-group, it was converted by the action of water and nitrous acid into nitrotoluene. The body so obtained was found to be identical with *metanitrotoluene*, and the toluidine from this identical with *metatoluidine*.

The result of the author's observations may be rendered as follows:—On substitution of hydrogen in the acetyl-derivative of para- or meta-toluidine, the hydrogen in the ortho-position is replaced; in ortho-toluidine replacement of the hydrogen in the meta-position is effected.

3. *Orthoiodotoluene*, $C_6H_4I_o.CH_3$, from ortho-toluidine. A colourless liquid, of exactly the same boiling point (204°) as metaiodotoluene, and of the same specific gravity (1·698). It is also not converted into an acid by oxidation, which is remarkable, since orthochloro- or bromo-toluene readily yield the substituted benzoic acids.

V. *Isomeric Tolylene-diamines.*

The existence of at least four nitrotoluidines has been established by previous experiments. Of these one is formed by the partial reduction of dinitrotoluene, the three others by nitration of the three isomeric toluidines.

1. *Para-meta-tolylenediamine*, p.m.$C_7H_6(NH_2)_2$. This is the known form obtained by reduction of dinitrotoluene. Hofmann gives 99° as its melting point, and about 280° as the boiling point. The sulphate, $C_7H_6(NH_2)_2.H_2SO_4 + 2aq.$, crystallises from water in long, prismatic, glistening crystals, which do not lose their water of crystallisation over sulphuric acid; 100 parts of water at 19·5° dissolve 5·58 parts of salt.

2. *Para-ortho-tolylenediamine*, p.o.$C_7H_6(NH_2)_2$. This modification is obtained by reduction of nitroparatoluidine with tin and hydrochloric acid. The solution is freed from tin by hydrogen sulphide, and evaporated to dryness; the residue, intimately mixed with pulverised caustic lime, is then distilled from a combustion-tube. It is obtained in brilliant white scales, which melt at 88·5°, and distil unchanged at 265°. It is moderately soluble in cold, more soluble in hot water. The

aqueous solution of the base is extremely unstable, becoming black after standing a few hours. The hydrochloride crystallises in long needles, extremely soluble in water. The sulphate, $C_7H_6(NH_2)_2.H_2SO_4+1\frac{1}{2}aq.$, forms magnificent, brilliant white, glistening scales; 100 parts of water at 19·5° dissolve 9·29 parts of salt. Both the free base and its salts become oxidised, when exposed to the air, much more readily than parametatoluylenediamine and its salts.

3. *Meta-ortho-toluylenediamine*, m.o.$C_7H_6(NH_2)_2$. Nitrometatoluidine is attacked with great energy by tin and hydrochloric acid. The free base is colourless and crystalline; it melts at 80°, and boils constantly and unchanged at 270°. It is even less stable, when exposed to the air than para-ortho-toluylenediamine. The sulphate, $C_7H_6(NH_2)_2.H_2SO_4$, is anhydrous and pulverulent, difficultly soluble in cold, more so in hot, water. 100 parts of water at 11·5° dissolve ·84 parts of salt.

The following is a tabular arrangement of the characteristics of the isomeric toluylenediamines:—

	Para-Meta.	Para-Ortho.	Meta-Ortho.
Melting point	90°.	88°·5	80°.
Boiling point	280°.	265°.	270°.
The H_2SO_4 salt forms.....	Long prisms.	Scales.	A powder.
The H_2SO_4 salt contains	$2H_2O$.	$1\frac{1}{2}H_2O$	——
The H_2SO_4 salt 100 pts. H_2O .. dissolve.....	5·58 pts. at 19·5°.	9·29 pts. at 19·5°.	0·84 pts. at 11·5°.

H. E. A.

On the Action of Sodium on the two Isomeric Monobromotoluenes. By W. Louguinine.*

The author describes the results he has obtained in the investigation of the action of sodium on solid and liquid monobromotoluene, in consequence of Th. Zincke's† notice on the same subject, to whom he relinquishes the further study of the isomeric ditolyls and their oxidation-products.

In the main his results are the same as Zincke's. He has employed light petroleum oil—B.P. 60°—100°—as solvent for both the solid and liquid bromide, having found the reaction to be less violent than when anhydrous ether was employed. About three days were required for the conversion of 100 grams of the solid bromide. The products of the reaction are: much regenerated toluene; a relatively large quantity of crystals, melting at 117°—119°, which remain liquid until 96°, and then suddenly solidify. These the author at first held to be stilbene, but he

* Deut. Chem. Ges. Ber., iv, 514. † Page 510 of this volume.

is now led by Zincke's communication to believe that they are solid ditolyl. Together with the crystals, a quantity of an oil of aromatic odour was obtained, which was freed from the last traces of crystals by refrigeration in a mixture of ice and salt; this boiled, after several rectifications, between 277° and 288°, and gave numbers agreeing with the formula $C_{14}H_{14}$. The monobromotoluene employed was dry and solid at the ordinary temperature, and could contain but traces of its liquid isomeride; it therefore seems impossible that the above liquid ditolyl is derived from liquid monobromotoluene. Considerable quantities of condensation-products were also always formed, which solidified to a black glistening mass. The yield of crystals and liquid ditolyl was always slight; about 10 grams of the former and 3 grams of the latter were obtained from 200 grm. solid bromide.

The liquid monobromotoluene employed was prepared from the original mixture of bromides boiling at 182°—183°, from which the solid bromide was separated by refrigeration, in a mixture of ice and salt, seven to eight times repeated. It then boiled constantly at 180°·5—181°. Sodium was found to have no action at the ordinary temperature on liquid bromotoluene dissolved in its own volume of petroleum oil, reaction taking place only when the mixture was heated on the water-bath to 50°; gas was also evolved, which was not observed in the case of the solid bromide, the quantity increasing with the temperature. The reaction is terminated at this temperature in about six days; the products are regenerated toluene; an oil boiling above 200°; and a solid residue, but this in less quantity than from the solid bromide. The oil deposited a small quantity of crystals of the same melting point and outward appearance as the above, probably also resulting from a trace of solid bromide still present. The oil distilled for the greater part between 272°—277°, or slightly lower than the liquid ditolyl obtained as bye-product from the solid bromide. It was not analysed, but the author regards it as liquid ditolyl, on account of its forming the main product of the reaction.

Finally, the author has sought to purify liquid monobromotoluene by a method based on the above observation, that it is unattacked by sodium at ordinary temperatures, whereas the solid is strongly acted upon. The greater portion of the solid was first removed from the mixture by thrice repeated refrigeration, the liquid portion was then dissolved in thrice its volume of oil, and one-quarter the quantity of sodium necessary to decompose it entirely, was added. The sodium was much acted on after standing over night; the liquid was decanted and distilled, and again similarly treated. At the fourth repetition of this operation the sodium remained bright, and the liquid clear, even after standing for five days. The boiling point of the body thus purified was 180·5°—181°. H. E. A.

On Isomeric Dibromotoluenes. By E. WROBLEWSKY.*

BY the action of bromine on solution of metatoluidine, there is produced, as the author has previously shown, a dibromotoluidine containing one of the bromine-atoms in the ortho position: by the action of alcoholic nitrous acid on this compound, a dibromotoluene is obtained crystallising in very beautiful long needles, almost insoluble in water, not very soluble in alcohol, of B.P. 239°, and M.P. 42·5°; it yields a nitro-dibromo-toluene of M.P. 59°.

By similarly treating paratoluidine, another dibromotoluidine is obtained yielding with nitrous acid a dibromotoluene, crystallising in fine long needles, of B.P. 241°, M.P. 60°, and giving a nitro-dibromotoluene of M.P. 124°.

Five out of the six dibromotoluenes existing, according to the benzene nucleus theory, are now known: the variety $(a) = 1, 2, 4$ has been obtained by the author from the perbromide of orthobromoparatoluidine: Fittig's dibromotoluene is $(b) = 1 : 2 : 4$: a third was obtained by the author from the perbromide of orthobromometatoluidine; this is either $(c) = 1 : 2 : 3$, or $(d) = 1 : 2 : 5$: the first dibromotoluene mentioned in this paper is either (c), (d), or $(e) = 1 : 2 : 6$, whilst the fifth body is that mentioned above, as produced from dibromoparatoluidine, and is either (c), (d), or (e); the one yet remaining to be discovered, therefore, is $(f) = 1 : 3 : 5$. Probably the one from dibromoparatoluidine is (e), whilst that from dibromometatoluidine is (d).

Attempts to obtain (f), which corresponds in structure to mesitylene, are already in progress.

C. R. A. W.

Researches on the Constitution of the Benzene Derivatives. By V. v. RICHTER.†

BY replacing in benzene two hydrogen-atoms by other monad radicals, three isomeric modifications can be obtained. Of these the constitution of the three phthalic acids is best known, and if we want to determine the constitution of any other bi-substituted benzene, it ought to be transformed either directly or indirectly into one of these three acids. The conclusions drawn from such a transformation are, however, not quite decisive, as it is well known that such compounds may be easily converted into other isomeric modifications. Kekulé has shown that this is the case with the sulpho-benzenic acids. Another example is afforded by the dibromobenzene, which is obtained by the direct action of bromine upon benzene, and, according to Meyer, is a para-compound, inasmuch as he succeeded in converting it into terephthalic

* Zeitschr. f. Chem. [2], vii, 209. † Deut. Chem. Ges. Ber., iv, 459—468.

acid. On the other hand, the same dibromobenzene is obtained by acting with phosphorus pentabromide on bromophenol, which appears to be an ortho-compound, as Koerner transformed it into common bromobenzoic acid. The author believes that the latter view is the correct one. By acting with nitric acid upon bromobenzene, he obtained bromonitrobenzene, which melts at 125°; this was converted by means of tin and hydrochloric acid into bromamidobenzen, which crystallises in octohedrons melting at 61°—62°.

Its nitrate, which forms long straight needles, readily soluble in hot, sparingly in cold water, was treated with nitrous acid, and bromine-water was added to the solution. The precipitated diazoperbromide was decomposed by boiling absolute alcohol, and thus a dibromobenzene was obtained identical with that formed by the direct action of bromine on benzene. This reaction again shows that dibromobenzene belongs to the ortho-compounds, because the bromonitrobenzene from which it was produced can also be obtained from nitraniline, which by reduction and subsequent oxidation yields quinone. This is further proved by the fact that when bromonitrobenzene is heated with caustic potash in sealed tubes, orthonitrophenol is formed.

From these experiments it follows that *one* transformation is not sufficient to decide the constitution of one of these compounds, and it is only when three isomerides are converted by analogous reaction into other isomeric compounds, that we are justified in considering their constitution as known.

As we know very little about the connection between the phenol and benzene derivatives on the one hand, and the substituted toluenes and benzoic acids on the other, it appeared of importance to obtain substituted benzoic acids from the three bromo- and chloronitrobenzenes. This may be effected by acting on the latter compounds with potassium cyanide, when the following reaction takes place:—

$$C_6H_4\left\{\begin{matrix}Br\\NO_2\end{matrix}\right. + CNK = C_6H_4\left\{\begin{matrix}Br\\CN\end{matrix}\right. + NO_2K.$$

The nitro-compounds have to be heated with *pure* potassium cyanide and alcohol to 180°—200°, and sometimes higher. After the reaction is finished, the tubes contain a sublimate of ammonium carbonate, and on opening them a large quantity of ammonia escapes. The dark-coloured contents (containing potassium nitrite) are boiled with alcoholic potash as long as ammonia escapes, then diluted with water and filtered, and the acid is precipitated with hydrochloric acid. For purification it is dissolved in ammonium carbonate, and treated with animal charcoal, this process being repeated until the acid appears perfectly white.

Bromonitrobenzene, melting at 125°, yields at 180° large quantities of *orthobromobenzoic* acid.

Bromonitrobenzene, melting at 56°, which was prepared from binitrobenzene by Griess's method, yields also easily *metabromobenzoic* acid.

Bromonitrobenzene, melting at 36°, is *not acted upon* by potassium cyanide, even at 280°.

Quite similar results were obtained with the chloronitrobenzenes. That melting at 84° gave at 200° *orthochlorobenzoic acid;* that which melts at 46° had to be heated to 250°—270°, and yielded *chlorosalylic acid* (metachlorbenzoic), whilst the liquid chloronitrobenzene was not acted upon at all. This shows that the nitro-group is not acted upon in the para-compounds.

The metabromobenzoic acid obtained from bromonitrobenzene melting at 56° may also be prepared from anthranilic acid (metamido-benzoic acid) by adding a little water to its nitrate and passing nitrous acid in until all the salt is dissolved. On adding bromine-water to its solution the diazoperbromide separates in hard red crystals. By adding alcohol to it, evaporating, and boiling the residue with alcoholic potash, in order to decompose the ether of the metabrombenzoic acid, a solution is obtained from which hydrochloric acid precipitates impure metabrombenzoic acid, which is purified in the same way as the acid obtained from bromonitrobenzene. It melts at 137° and sublimes in flat needles. Its most characteristic salt is the barium salt, $(C_7H_4BrO_2)_2Ba$, which is very soluble in water, whilst the salts of the two other isomeric acids are much less soluble. The calcium salt $(C_7H_4BrO_2)_2Ca + 2H_2O$ forms crystalline crusts. By fusing metabrombenzoic acid with caustic potash, salicylic acid is formed.

The nitro-compounds and the nitrous ethers are generally regarded as having quite a different constitution; but Mendelejeff has already pointed out that the difference in their reactions might as well be produced by the differently constituted groups with which they are combined. Just as chlorine behaves differently in C_2H_5Cl and in C_6H_5Cl, or in $C_6H_5.CH_2Cl$ and in $C_6H_4Cl.CH_3$, so will the group NO_2 show different reactions in the nitrous ethers and in nitro-compounds. The author has found that potassium cyanide acts on nitro-ethane (ethyl nitrite), forming potassium nitrite, and a fatty acid, which appeared to be propionic acid, but which was not obtained in a quantity sufficient for analysis.

C. S.

On a New Series of Aromatic Hydrocarbons. By TH. ZINCKE. PART II.*

Diphenylmethane or *Benzylbenzene*† is only slowly acted upon by a boiling solution of 2 parts of potassium dichromate, 3 of sulphuric acid,

* Deut. Chem. Ges. Ber., iv, 509—514. † See page 508 of this Journal.

and 9 of water. The product is an oily liquid, which on standing solidifies into a crystalline mass. After being well pressed, the crystals melt at 26°—26°·5, forming a clear liquid, which boils constantly at 300°, and on cooling solidifies to oblique, shining, transparent prisms. This body is benzophenone, $C_6H_5-CO-C_6H_5$, identical with that obtained from calcium benzoate.

On boiling *benzyl-toluene*, $C_6H_5-CH_2-C_6H_4-CH_3$, with chromic acid solution, the first product formed is *methyl-benzophenone*, the greater part of which is further oxidized to *benzoyl-benzoic acid* before all the hydro-carbon is attacked.

Methyl-benzophenone, $C_6H_5-CO-C_6H_4-CH_3$, is an oily liquid with a faint aromatic smell, and boiling at 307°—312°.

On adding an acid to a cold solution of one of its salts, the benzoyl-benzoic acid, $C_6H_5-CO-C_6H_4-CO_2H$, separates as a gelatinous precipitate; from a hot solution it is obtained in the form of small silky needles. It is sparingly soluble in cold water, in chloroform, benzene, and toluene, a little more in hot water; in ether, alcohol, and glacial acetic acid it dissolves readily, less easily in dilute alcohol. From hot dilute alcohol or chloroform it crystallises in thin plates having a satiny lustre; from dilute acetic acid it separates in thin long needles. It melts at 194°—195°, and sublimes at a higher temperature in large needles resembling very much sublimed benzoic acid. The barium salt, $(C_{14}H_9O_3)_2Ba + H_2O$, crystallises from a hot aqueous solution in ramified needles, which become anhydrous at 150°—160°. On evaporating a saturated solution, the salt crystallises in anhydrous plates. The *calcium salt*, $(C_{14}H_9O_3)_2Ca + 2H_2O$, crystallises in needles like the barium salt, but is more soluble. The silver salt, $C_{14}H_9O_3Ag$, is a white precipitate, soluble in large quantities of hot water.

Benzoyl-benzoic acid is at the same time a ketone. On boiling its alcoholic solution with zinc and hydrochloric acid, it takes up hydrogen, being converted into *benzhydryl-benzoic acid*, $C_2H_5-CH-OH-C_6H_4-CO_2H$, which is much more readily soluble in water and dilute alcohol than benzoyl-benzoic acid. It crystallises in ramified needles, melts at 164°—165°, and is decomposed at a higher temperature. By oxidising agents it is again easily converted into benzoyl-benzoic acid. The barium salt, $(C_{14}H_{11}O_3)_2Ba$, forms long hard needles grouped in stars: the calcium salt, $(C_{14}H_{11}O_3)_2Ca + 3H_2O$, crystallises in white needles resembling wavellite. The silver salt, $C_{14}H_{11}O_3Ag$, is a white precipitate sparingly soluble in boiling water.

Benzhydrylbenzoic acid has the same composition as benzilic acid, but these two acids are not identical, as an exact comparison showed.

When benzhydrylbenzoic acid is heated with concentrated hydriodic acid to 150° for some hours, it is transformed into *benzyl-benzoic acid*, $C_6H_5-CH_2-C_6H_4-CO_2H$, which is also obtained, besides other pro-

ducts, by acting on the hydrocarbon with dilute nitric acid. This acid is sparingly soluble in cold water; from a hot solution it crystallises in microscopic needles; from dilute alcohol in larger needles or plates with a satiny lustre. It melts at 154°—155°, and sublimes like benzoyl-benzoic acid.

The barium salt, $(C_{14}H_{11}O_2)_2Ba$, is sparingly soluble, and forms crystalline crusts. The calcium salt, $(C_{14}H_{11}O_2)_2Ca$, has similar properties, and the silver salt is a white precipitate. By oxidising agents it is again converted into benzoyl-benzoic acid. On subjecting the calcium salt to distillation, diphenylmethane is formed.

C. S.

Pyrene. By C. Graebe.*

The author has already communicated some of the results of his researches on pyrene to the Berlin Chemical Society,† and now publishes the details of his experiments. He prefers to prepare the picric acid compound, employed as a means of purifying the crude pyrene, by mixing *cold* alcoholic solutions of the two substances, when it is at once precipitated in the pure state. *Pyrene picrate*, $C_{16}H_{10} + C_6H_2(NO_2)_3OH$, crystallises from hot alcohol in long glistening red needles, which are but very slightly soluble in the cold. It is much more soluble in ether and carbon bisulphide, and readily soluble in benzene. It can be boiled with very dilute alcohol without undergoing change, but hot water slowly decomposes it. Alkalis and ammonia remove the picric acid, and the hydrocarbon thus obtained distils unchanged at a temperature somewhat above 360°, melts at 142°, and crystallises from benzene or ether in rather large rhombic tables.

Nitropyrene, $C_{16}H_9NO_2$. Pyrene is heated for two hours with a mixture of equal volumes of nitric acid, sp. gr. 1·2, and water, when it melts to a reddish oil which solidifies on cooling. This, after being purified by crystallisation from hot alcohol, yields yellow needles melting at 140° to 142°. They are only slightly soluble in cold alcohol, somewhat more so in hot alcohol, and easily in ether and benzene.

Dinitropyrene, $C_{16}H_8(NO_2)_2$, is obtained by boiling pyrene with nitric acid, sp. gr. 1·45, extracting the nitropyrene formed at the same time by boiling the product with alcohol, and finally crystallising from glacial acetic acid. It forms slender yellow needles, which are but slightly soluble in alcohol, ether, or benzene. *Tetranitropyrene*, $C_{16}H_6(NO_2)_4$, is formed when dinitropyrene is boiled for a long time

* Ann. Chem. Pharm., clviii, 285—299.

† Deut. Chem. Ges. Ber., iii, 738, and this volume, p. 117.

with nitric acid, sp. gr. 1·5, and crystallises in lustrous needles from glacial acetic acid, in which it is slightly soluble. It is almost insoluble in alcohol, and but very slightly so in ether and benzene. It melts at about 300°.

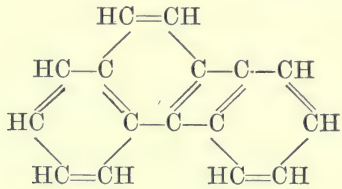
Dibrompyrene dibromide, $C_{16}H_8Br_2.Br_2$. On exposing finely divided pyrene to the vapour of bromine in excess, it is absorbed, and the product, when purified by crystallisation from boiling nitrobenzene, forms pale yellow needles. These are almost insoluble in alcohol, ether, and benzene, but dissolve readily in aniline and nitrobenzene. *Tribromopyrene*, $C_{16}H_7Br_3$, separates in the solid state on adding a slight excess of bromine to a solution of pyrene in carbon disulphide, hydrobromic acid being evolved at the same time. It crystallises from nitrobenzene in colourless needles, which may be freed from the solvent by washing with ether. It is almost insoluble in alcohol, ether, and carbon bisulphide, somewhat more soluble in benzene, and readily so in hot nitrobenzene and aniline.

Pyrene-quinone, $C_{16}H_8(O_2)''$. When solid chromic acid is added to a hot solution of pyrene in glacial acetic acid, a strong reaction sets in, with formation of pyrene-quinone. This compound separates in great part during the reaction, and the rest may be thrown down by the addition of water to the solution. After being washed with water and recrystallised from glacial acetic acid, it forms red needles or prisms. The addition of water to the acetic acid solution precipitates it as a brick-red powder, which is very slightly soluble in alcohol, ether, benzene, and carbon bisulphide, but very easily in nitrobenzene. It dissolves in concentrated sulphuric acid with a brown colour, and when heated with zinc-dust is reconverted into pyrene.

Hexhydropyrene, $C_{16}H_{16}$. Pyrene in alcoholic solution is not acted upon by sodium amalgam, and even when heated to 150° with amorphous phosphorus and strong hydriodic acid (boiling at 127°) it is only partly converted into hydropyrene. On heating the mixture, however, to 200° for eight or ten hours, the whole of the pyrene becomes hydrogenised, and the product may be purified by repeated crystallisation from alcohol. Hexhydropyrene crystallises in needles or prisms which melt at 127°, and are very soluble in ether, benzene, and boiling alcohol, but less so in cold alcohol. It does not form a compound with picric acid, and when passed through a red hot tube, is again converted into pyrene. Other more highly hydrogenised compounds are formed along with hexhydropyrene, but the author has not been able to isolate them.

Constitution of Pyrene. From the behaviour of pyrene towards chromic acid and nitric acid, it would appear that it does not contain any lateral chains, but consists of a closed system of carbon atoms, and is therefore analogous in its structure to naphthalene and anthra-

cene. The author believes it to be phenylene-naphthalene, $C_{10}H_6(C_6H_4)$, and represents its structure thus :—



C. E. G.

Chrysene. By C. LIEBERMANN.*

THE chrysene employed in this research was extracted from the mixture of solid hydrocarbons which have a higher boiling point than anthracene, and form the latter portion of the distillate from coal tar. By treating this mixture with successive quantities of cold carbon bisulphide, the pyrene and similar hydrocarbons are dissolved, leaving 18 to 19 per cent. of a yellow powder melting at 240°. By crystallising this from coal-oil (boiling at 150°) the chrysene is obtained in bright yellow glistening scales, from which the colour cannot be completely removed, even by repeated crystallisation from ether, or by the insolation of its solutions. It is however obtained colourless by heating the yellow crystals with hydriodic acid and amorphous phosphorus to 240°; also by boiling them with alcohol and a small quantity of nitric acid. It cannot be sublimed without decomposition, and when submitted to distillation in a current of gas, its fusing point is lowered sometimes as much as 10°. Chrysene, $C_{18}H_{12}$, is very slightly soluble in cold alcohol, ether, benzene, or glacial acetic acid, but somewhat more so in carbon disulphide. It is moderately soluble in hot coal-oil of high boiling-point, and in boiling glacial acetic acid, from both of which it separates in the crystalline state on cooling. It melts at 248° to 250°, and its boiling point lies above the range of the mercurial thermometer. The yellow chrysene dissolves in a large quantity of hot sulphuric acid, with a dirty violet colour, forming sulpho-acids, whilst colourless chrysene forms a pure blue solution. Chlorine acts upon it very little in the cold, but on heating a substance is formed which sublimes in white needles with partial decomposition. It forms a picric acid compound, $C_{18}H_{12}.C_6H_2(NO_2)_3OH$, crystallising in orange coloured needles, which are decomposed by the action of cold alcohol, being converted into pseudomorphs of chrysene. The author believes

* Ann. Ch. Pharm., clviii, 299—315.

the substances described by Williams*, Galletly,† Robiquet and Colin,‡ Pelletier and Walter,§ Laurent,‖ and Berthelot to be more or less pure chrysene.

Mononitrochrysene, $C_{18}H_{11}NO_2$. When yellow chrysene is boiled with alcohol and a little nitric acid of sp. gr. 1·4, the solution slowly acquires an orange colour from formation of nitrochrysene, and after 24 hours' digestion is separated from unaltered chrysene concentrated by distillation, and allowed to cool. The liquid is now filtered from chrysene and a little nitrochrysene, and on the addition of water, an orange-red precipitate of nitrochrysene is formed, which may be purified by crystallisation from boiling alcohol. The chrysene remaining undissolved in the above operation is much less readily acted upon by nitric acid than before, and when boiled with potash and recrystallised, yields colourless chrysene.—*Tetranitrochrysene*, $C_{18}H_8(NO_2)_4$. On dissolving chrysene in fuming nitric acid in the cold, and adding water after some hours, this substance is precipitated as a yellow, difficultly soluble powder. By treatment with chromic acid, tetranitrochrysene is in great part destroyed, and when heated to 170° with nitric acid, it forms a volatile acid containing nitrogen.

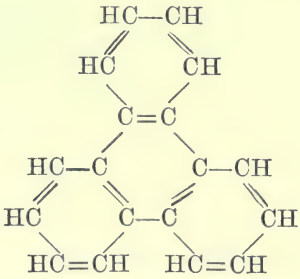
Bromochrysene. On adding bromine to chrysene suspended in carbon bisulphide, hydrobromic acid is evolved, and a substance obtained which crystallises from benzene in colourless needles. The analyses indicated a mixture of dibromochrysene and tribromochrysene.

Chrysoquinone, $C_{18}H_{10}(O_2)''$. On oxidising crystallised chrysene suspended in glacial acetic by the careful addition of one and a half times its weight of chromic acid, and finally heating to boiling to complete the reaction, a solution is obtained from which the quinone may be precipitated, by the addition of water, as an orange-red powder. In order to purify this, it is dissolved in concentrated sulphuric acid, filtered through asbestos to separate unaltered chrysene, and precipitated by water. Repeated crystallisations from benzene render it quite pure. It is moderately soluble in hot alcohol, benzene, and glacial acetic acid, and crystallises from the former in long rhombic plates. It is but slightly soluble in ether and carbon bisulphide, melts at about 220°, and when more strongly heated, sublimes with partial decomposition. It is soluble in cold concentrated sulphuric acid, with a fine pure blue colour, which is very characteristic, and is precipitated unchanged by the addition of water. Chrysoquinone yields phthalic acid when treated with potassium permanganate, or by the prolonged action of chromic acid. When it is heated with zinc-powder, chrysene is regenerated.—*Chrysohydroquinone*. On boiling the quinone with

* J. pr. Chem. lxvii, 248.
† Chem. News, x, 243.
‡ Ann. Chim. Phys., iv, 326.
§ Ann. Chim. Phys., ix, 89.
‖ Ann. Chim. Phys., lxvi, 136, and lxxii, 415.

zinc-powder and caustic potash-solution, it dissolves to a yellow solution, from which acids precipitate colourless flocks of chrosohydroquinone, which can be easily reoxidised to the quinone. This change takes place when it is heated to 200° with access of air, or by dissolving it in concentrated sulphuric acid and agitating it with air, when the solution acquires the characteristic blue colour of the chrysoquinone.—*Dichlorochrysoquinone* and *Decachlorochrysene.* When one molecule of chrysene is heated for a short time to 200° with two molecules of phosphoric chloride and an excess of phosphorus oxychloride, a green uncrystallisable substance is formed, which is soluble in carbon bisulphide and phosphorus oxychloride, but almost insoluble in alcohol, ether, and benzene. The contents of the tubes, when gradually added to alcohol, give a bright yellow flocculent precipitate of dichlorochrysoquinone, $C_{18}H_8Cl_2O_2$. On heating chrysoquinone for twelve hours to 220° with a large excess of phosphoric chloride, it is converted into decachloro-chrysene, $C_{18}H_2Cl_{10}$, a yellowish-red uncrystallisable substance, soluble in carbon bisulphide. — *Tetranitrochrysoquinone,* $C_{18}H_6(NO_2)_4O_2$. Chrysoquinone dissolves in cold concentrated nitric acid, and after it has been allowed to stand for some hours, water precipitates tetranitrochrysoquinone as an orange-yellow powder, which is but little soluble in most menstrua. It deflagrates slightly when heated.

The consideration of the derivatives of chrysene, and its conversion into phthalic acid by oxidation, clearly show that it is a member of the naphthalene-anthracene series, and moreover the absence of any fatty group is rendered manifest by the formation of the quinone and its reconversion into chrysene. Strecker has pointed out* that its constitution is probably analogous to that of naphthalene and anthracene, and if the substance prepared synthetically from benzene by Berthelot† be identical with chrysene, its structure might be represented thus:—



C. E. G.

* Lehrbuch der Organ. Chem., 762. † Bull. Soc. Chim., vi, 276.

On Mono- and Di-nitronaphthalene. By F. BEILSTEIN and A. KUHLBERG.*

MONO-NITRONAPHTHALENE is best obtained by the action of nitric acid on naphthalene in the cold: it is easily soluble in carbon bisulphide, less easily in alcohol; crystallises in shining sulphur-yellow needles; melts at 58°·5.

When α-dinitro-naphthalene melting at 212° is dissolved in alcohol, a little strong ammonia added, and a weighed quantity (3 molecules) of hydric sulphide passed in, nitro-amido-naphthalene is produced (C. S. Wood finds that boiling ammonium sulphide reduces further to ninaphthylamine $C_{10}H_8N_2O$). The sulphate is but little soluble in water, and contains $[C_{10}H_6(NO_2)(NH_2)]_2H_2SO_4 + 2H_2O$, the water of crystallisation being lost over sulphuric acid. The free base is crystallisable from water and melts at 118°—119°. The nitrate gives a diazo-derivative, which, on decomposition by alcohol, gives nitro-naphthalene identical in melting point and solubility in alcohol with that described above; whence it is concluded that α-dinitronaphthalene has the two NO_2 groups symmetrically disposed.

α-dinitro-naphthalene is not attacked by potassium dichromate and sulphuric acid, even when very concentrated and after long action.

C. R. A. W.

On Olibanum. By A. KURBATOW.†

BY distillation with water in a cast iron retort, an oil is obtained constituting about 7 per cent. of resin taken; alcohol extracts from the residue in the retort about 72 per cent. of resin, and the remainder is gum. The crude oily distillate boils between 160° and 170°, and contains oxygen, as Stenhouse previously observed (B.P. 162 according to Stenhouse); by fractional distillation a hydrocarbon, *Olibene*, of boiling point 156°—158°, turpentine-like odour, and sp. gr. 0·863 at 12° is obtained, and a small quantity of an oxidized substance boiling above 175°, and not furnishing a hydrocarbon by treatment with sodium. Olibene is soluble in alcohol and ether, and is resinised by nitric acid; it absorbs one molecule of hydrogen chloride, giving on standing a crystalline camphor-like body $C_{10}H_{16}.HCl$, which melts at 127°.

The resin extracted as above by alcohol melts readily, and yields on dry distillation, traces of an organic acid, and an oil which boils above 360°, and contains less oxygen than the resin itself.

C. R. A. W.

* Zeitschr. f. Chem. [2], vii, 211. † Zeitschr. f. Chem. [2], vii, 201.

On the Action of Chlorine on Ethyl Chloride. By WILHELM STAEDEL.*

BY a very large number of fractional distillations of 5000 grams of the crude product of the action of chlorine on ethyl chloride, it was found that ultimately only between 3 and 4 grams were obtainable, boiling between 80° and 90°, whence it is concluded that ethylene chloride was not among the products of the reaction; small quantities of pure mono- and di-chlorinated ethyl chloride were separated, boiling constantly at 62° and 74·5° respectively.

The different results recently obtained by Geuther are explicable as the supposition that his ethyl chloride contained alcohol, from which the ethylene chloride was formed.

Regnault has found the boiling point of mono-chlorinated ethyl chloride to be 64°, Geuther 57°—59°, while Beilstein and also Krämer have found it to be 60°; of these researches Krämer's deserves the most confidence, as he operated on larger quantities.

C. R. A. W.

Action of Phosphorus Pentachloride on Chloral-ethyl-alcoholate. By LOUIS HENRY.†

THE author has described,‡ as the product of this reaction, a body of the constitution $CCl_3—CHCl—OC_2H_5$, which corresponds in composition to a tetrachlorinated-ethyl-ether. O. Jacobsen,§ in his paper on the chloro-substitution products of ethyl oxide, when speaking of tetrachlor-ethyl oxide, remarks that the compound obtained by Henry is no doubt identical therewith, but that it is extremely improbable that his body should permit, as stated by him, of being washed with water, and even with soda, and finally repeatedly distilled at 185°—190° without undergoing decomposition.

In the present notice the author upholds his former statements as to the stability of the compound in question, and quotes details of preparation and purification, having also repeated his former experiments.

115 grm. chloral-alcoholate were acted upon at one operation; the phosphorus oxychloride in the crude product decomposed by water, and the oily residue, after washing with solution of sodium carbonate and drying over calcium chloride, submitted to rectification. At first hydrochloric acid is evolved, and a small quantity of an acid distillate is obtained, but the product passing over is soon neutral; but little distils below 180°, the greater portion between 185°—195°; at the close of

* Zeitschr. f. Chem. [2], vii, 197.
† Deut. Chem. Ges. Ber., iv, 435.
‡ Ibid., 101.
§ Ibid., 215.

the operation the thermometer rises to 210°, and a slight carbonaceous residue remains. The pure body, obtained after several rectifications of the portion boiling between 185°—195°, boils at 188°—190° (uncorrected) under a pressure of 755 mm. and distils without leaving any residue. It is extremely sensitive to the action of water; exposed to moist air, or in contact with water, it rapidly becomes acid; decomposition, however, takes place very slowly both in the cold and on warming, and even after heating with an equal volume of water in a sealed tube to 100° for several hours, the greater part remained undecomposed. Three chlorine determinations gave respectively 66·13, 67·09 and 66·36 per cent., the theoretical percentage being 66·98. Its vapour-density, determined by Hofmann's method in aniline vapour, was found to be 7·398, calculated 7·705.

The author further holds, as against the opinion of Jacobsen, that the properties described by him as characteristic of the tetrachlorethyl oxide are by no means improbable, but quite natural, when it is considered that it is intermediate between trichlorinated-acetal, $CCl_3—CH(OC_2H_5)_2$, and trichlorinated-ethylidene chloride, $CCl_3 - CHCl_2$, and should, therefore, resemble in properties the one or the other of these bodies. Further v. Meyer* has obtained the corresponding aceto-derivative, $CCl_3—CHCl—OC_2H_3O$, which he subjected to a much more energetic treatment in order to effect its purification.

H. E. A.

On the Constitution of Allyl-compounds. By FRIEDRICH GEROMONT.†

ALLYL bromide is admitted to have the structural formula $CH_2=CH—CH_2Br$, *i.e.*, it does not contain methyl: by the addition of the elements of hydrobromic acid, two bodies might be produced, viz., propylene bromide (methyl-ethylene bromide) $CH_3—CHBr—CH_2Br$, and tri-methylene bromide $CH_2Br—CH_2—CH_2Br$.

By heating highly concentrated hydrobromic acid and allyl bromide in a sealed tube to 100° for a few minutes, almost the whole of the allyl bromide becomes converted into a mixture of two isomeric bodies of formula $C_3H_6Br_2$, separable by fractional distillation: one is propylene bromide, yielding with excess of alcoholic potash only allylene; the other boils at a higher temperature (160°—163° at 719 mm. uncorrected), and forms with alcoholic potash only allyl-ethyl-ether. This latter is trimethylene bromide; treated with glacial acetic acid and silver acetate, it yields trimethylene diacetate boiling at 203°—205° at 717 mm. uncorrected: with barium hydrate this compound yields trimethylene

* Deut. Chem. Ges. Ber., iii, 447. † Ann. Ch. Pharm. clviii, 369—371.

glycol, as a thick sweet-tasting liquid boiling between 208° and 218; evidently this is the alcohol of ethylene-lactic acid and malonic acid.

Experiments on the oxidation-products of this glycol, and on the possibility of forming trimethylene, $\begin{array}{c} CH_2 \\ / \quad \backslash \\ CH_2 - CH_2 \end{array}$ are in progress.

C. R. A. W.

On Naphthazarin. By A. A. de Aguiar, and Al. G. Bayer.*

In their previous communication† the authors suggested that the formation of naphthazarin from dinitronaphthalene possibly consisted in the direct elimination of nitrogen from the latter, and subsequent molecular re-arrangement. They have now endeavoured to test the correctness of their hypothesis by an analysis of the escaping gases, but do not find it in any way confirmed. 4 grams of dinitronaphthalene when heated with sulphuric acid to 200°, until entirely converted into naphthazarin, gave 450 c.c. gas, which contained 86·45 per cent. SO_2, 7·01 per cent. N, and 6·54 per cent. CO.

They further describe the black substance constantly obtained as a by-product, together with naphthazarin. Sulphuric acid only was used in all the experiments. The cooled product of the reaction was mixed with water, and the black precipitate filtered off from the blue-violet solution, and then repeatedly boiled with water acidulated with sulphuric acid; much ammonia thus went into solution. The product was now dissolved in soda-solution, again precipitated by sulphuric acid, the precipitate well washed with hot water, and then dried at 100°. Analysis of the product thus purified gave numbers corresponding to those required by trioxynaphthoquinone, $C_{10}H_3(HO)_3O_2$. The same body was obtained by the action of sulphuric acid on pure naphthazarin, its formation, in this case, being possibly in accordance with the equation:—

$$C_{10}H_4(HO)_2O_2 + SO_4H_2 = C_{10}H_3(HO)_3O_2 + SO_2 + H_2O.$$

Thus prepared it is amorphous, with a reddish metallic gloss; it cannot be sublimed; dissolves in alkalies with a dirty blue-violet colour, and tinges hot water pale-red. On reduction with zinc-dust it yields naphthalene.

In an operation in which the heating had been carried too far, a body was obtained, which, after purification in the same manner, gave on analysis less C. and H. than the above, and this the authors look upon as a mixture of tri- and tetra-oxynaphthaquinone.

The before-mentioned blue liquid exhibits a somewhat remarkable

* Deut. Chem. Ges. Ber., iv, 438. † This Journal, ix, 355.

behaviour. It yields, as is known, naphthazarin on boiling, but the same also takes place slowly in the cold, the colour changing to red. This blue solution certainly does not contain the ready-formed naphthazarin as such; but little ammonia can be detected in it; whereas, after boiling, a considerable quantity is present. After removal of the sulphuric acid from it by barium carbonate, a blue-violet neutral liquid is obtained containing barium; if this be acidified, it retains the blue colour, a sign that the colour is not due to naphthazarin held in solution by the carbonate. On heating, the colour changes to red, ammonia is formed and naphthazarin may be recognised by all its characteristic reactions. Whether this body, which is so difficult of isolation, is an azo- or amido- compound is a question; the latter seems the more probable, judging from the powerful reducing action exerted by sulphuric acid at 200°.

If the acidified liquid containing barium, or even the original blue-violet liquid, be allowed to stand for some hours, a second body separates, which differs both in the colour of its solutions and in other respects from the above. It also yields naphthazarin, but with much greater difficulty. Naphthazarin prepared by Roussin's process always contains a certain quantity of this body. In their former notice the authors quoted the analysis of a black body containing 6·46 per cent. of nitrogen; this probably consists for the greater part of one of the above-mentioned compounds.

H. E. A.

On Gallein. By A. Baeyer.*

This new colouring matter is produced by heating pyrogallic acid with phthalic acid, or, better, with phthalic anhydride, for some hours, to 190°—200°, until the mass becomes thick; on dissolving it in hot alcohol, filtering, and adding water to the filtrate, a precipitate of nearly pure gallein is obtained, which is easily purified by crystallisation from hot dilute alcohol. The crystals appear brown in reflected and blue in transmitted light; when the solution dries up, the residue is left as a mass with a greenish-yellow metallic lustre. It is almost insoluble in cold water; in hot water it is sparingly soluble with a red colour; in alcohol it dissolves freely, forming a dark-red solution. Ether also takes up a little, but the solution is colourless. Gallein bears a strong resemblance to hæmatein, the colouring principle of logwood; like the latter, it dissolves in caustic potash with a splendid blue colour, the solution soon assuming a dirty tinge, and in ammonia with a violet colour. The colours which it produces on cloth mordanted with iron and alumina, are finer and more stable than the logwood colours, and

* Deut. Chem. Ges. Ber., iv, 457—459.

resemble more those of barwood. Gallein is decomposed by heat like hæmatein, carbonisation taking place, and no sublimate being formed.

Gallein is obtained synthetically from pyrogallic acid, and hæmatein yields pyrogallic acid on fusion with caustic potash. Both are converted into colourless compounds by reducing agents, gallein yielding *gallin*, a body which is obtained in fine crystals, and, in contact with ammonia, is again oxidised to gallein, just as hæmatoxylin, under the same conditions, is reconverted into hæmatein. The exact formula of gallein has not yet been determined; it contains less hydrogen than hæmatein, $C_{24}H_{18}O_9$, to which body it is very closely related, and there cannot be any doubt that it belongs to the family of the colouring matters of logwood and barwood; it is the first body of this group obtained artificially.

Besides gallic acid, trimesic, pyromellitic, and prehnitic acids, and oil of bitter almonds also produce gallein when heated with pyrogallic acid; but terephthalic, benzoic, oxalic, and succinic acids are without any action. This shows that the phthalic acid is not used up in the reaction, which can only be an abstraction of water and perhaps also oxidation. Other dehydrating or oxidising agents, as sulphuric acid, zinc chloride, arsenic acid, nitro-benzene, yield, on fusion with pyrogallic acid, brown or black bodies, but no gallein.

But Wackenroder's gallerythroic acid, and Berzelius's cœrulo-gallic acid (*Blaugallussäure*), which are formed by treating gallic acid with alkalies, appear to be identical with gallein.

C. S.

On the Constitution of Æsculin. By HUGO SCHIFF.*

THE author confirms his former results, that by the action of acetic anhydride on æsculin *acetyl-æsculin*, $C_{15}H_{10}(C_2H_3O)_6O_9$, is formed, and that with aniline it yields *trianilæsculin*, $C_{15}H_{16}O_6(C_6H_5N)_3$.

On acting on *æsculetin* with acetic anhydride or acetyl chloride, crystalline *triacetylæsculetin*, $C_9H_3(C_2H_3O)_3O_4$, is formed, a body already obtained by Nachbaur. When æsculetin is heated with aniline to 200°, *trianilæsculetin*, $C_9H_6O(C_6H_5N)_3$, is obtained, a brown amorphous powder, which dissolves in alcohol with a red colour.

Paraæsculetin has the properties of an aldehyde, and reduces alkaline copper tartrate, indigo, silver-salts, &c., in the cold; aniline acts easily on it, forming also trianilæsculetin; but it gives no reaction with acetic anhydride. The above reaction may be explained by the following formulæ:—

* Deut. Chem. Ges. Ber., iv, 472—474.

Æsculetin. Paraæsculetin.

$$C_6H_2\left\{\begin{array}{l}CH.O\\C.OH\\C.OH\\OH\end{array}\right. \qquad C_6H_2\left\{\begin{array}{l}CH.O\\CH.O\\CH.O\\OH\end{array}\right.$$

For the formation of formic and protocatechuic acids by fusing æsculetin with caustic potash, we have the equation—

$$C_6H_2\left\{\begin{array}{l}CH.O\\(C.OH)_2\\OH\end{array}\right. + 2H_2O + O_2 = C_6H_3\left\{\begin{array}{l}CO{\cdot}OH\\(OH)_2\end{array}\right. + 2CH_2O_2.$$

The constitution of æsculin would then be—

$$C_6H_2\left\{\begin{array}{l}CH.O\\(CH.OH)_4\\CH_2\\O\\C.OH\\C.OH\\CH.O.\end{array}\right.$$

C. S.

Preliminary Notice on the Electrolysis of Substituted Derivatives of Acetic Acid. By G. E. Moore.*

At Prof. Kolbe's suggestion the author has subjected cyanacetic acid to electrolysis. As is well known, Kolbe obtained dimethyl by electrolysis of acetic acid, and, similarly, it was probable that substituted acetic acids would yield the corresponding substituted radicals. Thus, in the case of cyanacetic acid—

$$2\left\{\begin{array}{l}CH_2CN\\COOH\end{array}\right. + H_2O = (CH_2CN)_2 + 2CO_2 + H_2O + H_2.$$

The cyanacetic acid employed was pure and perfectly free from chlorine. On submitting a concentrated neutral solution of potassium cyanacetate to the action of the current from six Bunsen's elements, streams of gas were evolved at the positive pole, which was almost entirely absorbable by potash-solution; the residue is an indifferent gas, probably nitrogen. The strongly acid liquid in the positive cell, at the conclusion of the reaction, was then shaken up with much ether, and the latter distilled off on the water-bath. The solid, acid, deliquescent residue was redissolved in much ether, the solution neutralised with potash, filtered, and distilled on the water-bath. A brownish, solid residue was thus obtained, which, in external properties and melting point (37·8°) was identical with *ethylene dicyanide*. On heating it with potash, ammonia was evolved and a residue obtained in which the

* Deut. Chem. Ges. Ber., iv, 519.

presence of ethylene-succinic acid was proved, both by the irritating odour of its vapour and by the ferric chloride reaction.

At the same time, other products of decomposition are formed, the investigation of which is not yet concluded. The author also proposes to extend his experiments to the higher substituted acetic acids, *e.g.*, dichlor- and trichlor-acetic acids.

H. E. A.

Note on Isomeric Iodobenzoic Acids. By PETER GRIESS.*

IN his communication "On the constitution of Benzene Derivatives," V. v. Richter states his intention of preparing the hitherto undescribed iodosalylic acid. The author announces that he already obtained this acid, some five years ago, by the action of hydriodic acid on the sulphate of diazosalylic acid (from anthranilic acid). It crystallises in long white needles, which may be readily sublimed; is somewhat difficultly soluble in hot, very difficultly soluble in cold, water, but very easily dissolved in the cold, both by ether and alcohol. It melts at 152°. The melting point of the iodobenzoic acid, obtained by the action of hydriodic acid on diazobenzo-amidobenzoic acid, and previously described by the author, is 185°, or 33° lower than that of iodosalylic acid. He further remarks that he, at the same time, obtained, but did not describe, iododracylic acid from diazodracylic acid. Körner† has also, in the mean time, prepared iododracylic acid (paraiodobenzoic acid) by the oxidation of a modification of iodotoluene; his description of the properties of this body is entirely confirmed by the author.

H. E. A.

On Acetone-sulphonic Acid. By C. BENDER.‡

THE following are the results of the further examination of this acid and its salts by the author:—

Acetone-sulphonic acid was prepared from its potassium salt by decomposing that salt with an equivalent quantity of dilute sulphuric acid, and extracting with alcohol. The crude acid, left on distilling off the alcohol, was neutralised with lead carbonate, and the very soluble lead salt obtained was then decomposed by hydrogen sulphide. Thus purified it is a colourless, uncrystallisable syrup, from which the following salts were prepared:—

Barium acetonesulphonate, $(CH_3.CO.CH_2SO_3)_2\,Ba + aq$, crystallises in colourless, glistening scales. The air-dry salt loses a portion of its water when exposed over sulphuric acid; the whole at 100°.

* Ber. Deut. Chem. Ges., iv, 521. † Jahresb. 1867, 665.
‡ Ber. Deut. Chem. Ges., iv, 517.

Lead acetonesulphonate $(CH_3.CO.CH_2SO_3)_2Pb + aq$, crystallises in colourless, very soluble scales, which exhibit an acid reaction. It melts at 140°, and is entirely decomposed on heating to 170°.

Cupric acetonesulphonate, $3[(CH_3.CO.CH_2SO_3)_2Cu] + aq$. Blue-green, very soluble scales having an acid reaction.

Concentrated solution of potassium hydrate has no action on acetone-sulphonic acid, as the author formerly* supposed it had.

On heating a dry mixture of potassium acetonesulphonate and pure potassium cyanide, a volatile, crystalline body sublimes, which is insoluble in alcohol and ether, but soluble in water. A nitrogen determination in this compound gave 17·20 per cent.; the formula $CH_3.CO.CH_2.CN$, requires 16·86 per cent. It is to be expected that this cyanide will yield an acid of the constitution $CH_3.CO.CH_2.COOH$, homologous with pyruvic acid.

H. E. A.

On Grape-seed Oil. By A. Fitz.†

The seeds of the grape were found by the author to contain from 15 to 18 per cent. of a fat oil. This was saponified with potash, and the acids were separated by the partial precipitation of their alcoholic solution with lead acetate, the first fractions being flocculent, the later semifluid. The flocculent precipitate, on being treated with warm ether, left a small portion undissolved, the acid from which, by its melting point and analysis, proved to be a mixture of palmitic and stearic acids. The acid contained in the soluble lead salt crystallised from alcohol in lustrous needles, and on analysis was found to be erucic acid. The solubility of its lead salt varies extremely with the temperature, being very soluble in ether, benzene, or acetone when hot, and but slightly when cold. This accounts for the apparent discrepancy between the accounts given by Darby,‡ Websky,§ and Haussknecht,‖ and those of Otto.¶ One half of the mixed acids contained in the oil was found to be erucic acid, and the remainder an acid yielding a semi-fluid lead salt, together with a very small quantity of palmitic and stearic acids. By treatment with nitrous acid, the erucic acid was converted into the corresponding elaïdic acid, which melted at 56°. Websky and Haussknecht give 60° as the melting point of their brassidic acid. The lead salt is almost insoluble in warm ether.

Action of fused Potash on Erucic Acid.—When erucate of potassium was fused with potash, the soap separated by common salt, and then decomposed by hydrochloric acid, it gave a fatty acid melting at 73°,

* Zeit. f. Chem., 1870, 163.
‡ Ann. Ch. Pharm., lxix, 3.
‖ Ann. Ch. Pharm., cxliii, 41.
† Deut. Chem. Ges. Ber., iv, 442—446.
§ J. pr. Chem. lviii, 461.
¶ Ann. Ch. Pharm., cxxvii, 182.

the analysis of which corresponded with the formula of arachidic acid. In another experiment, the product obtained by fusing erucic acid with potash was distilled with dilute sulphuric acid, when acetic acid was obtained. Erucic acid, $C_{22}H_{42}O_2$, therefore, splits up, under the action of fused potash, into arachidic acid, $C_{20}H_{40}O_2$, and acetic acid, $C_2H_4O_2$. The author, in conclusion, points out the economic value of grape-seeds as a source of oil and of tannic acid, the latter of which would be of value in fining wines. C. E. G.

On Parasulphobenzoic Acid. By IRA REMSEN.*

IT has been previously shown by the author that crude potassium sulphobenzoate fused with caustic potash forms both oxybenzoic acid and paraoxybenzoic acid; he now finds that by decomposing the crude potassium salts of the mixed sulphobenzoic acids with sulphuric acid, evaporating, extracting of the free acids with alcohol, and converting them into barium salts, two entirely different barium salts are obtainable, one crystallising on cooling from the hot aqueous solution in fine needles, the other being obtained by evaporation of the mother liquors of the first,in beautiful monoclinic crystals.

Both salts gave numbers agreeing with the formula $(C_{14}H_{10}S_2O_{10})$ Ba $+ 3H_2O$; the first does not lose its water of crystallisation below 250° —260°, the second becomes anhydrous at 200°: in cold water the first is almost insoluble.

Converted into potassium salts and fused with caustic potash, these two substances yielded respectively paraoxybenzoic and oxybenzoic acids; the former acid agreed in all respects with that obtained by other processes, had the same crystalline form, contained water of crystallisation which it lost at 100°, and melted at 210°.

The principal product of the action of sulphuric acid on benzoic acid is usually metasulphobenzoic acid; the conditions necessary for the production of parasulphobenzoic acid in quantity are not as yet known.

C. R. A. W.

Note on Eugenol and Dimethyloxybenzoic Acid. By C. GRAEBE and E. BORGMANN.†

THE authors were induced to investigate the behaviour of potassium dichromate when heated with eugenol-methylether dissolved in glacial acetic acid, as the above oxidising mixture forms the best means for

* Zeitschr, f. Chem. [2], vii, 199. † Ann. Ch. Pharm., clviii, 282—284.

converting cresol-methylether into the corresponding methoxybenzoic acid.*

Accordingly, the colourless methylether boiling between 237°—339° obtained by heating eugenol-sodium with methyl iodide was dissolved in glacial acetic acid, and heated for two or three days on the water-bath with 2 parts of powdered potassium dichromate. It was then diluted with water, and ether added to separate any unchanged eugenol-methylether. The ethereal solution of the methoxybenzoic acid was shaken with a solution of ammonium carbonate, and the alkaline liquid concentrated. On the addition of an acid, a crystalline organic acid separated, which was recrystallised from hot water.

Analysis led to the formula $C_6H_3(OCH_3)_2(CO_2H)$.

Dimethoxybenzoic acid greatly resembles anisic acid; it is sparingly soluble in cold, easily soluble in hot water, and very easily in alcohol and ether. It crystallises and sublimes in glistening white needles, and melts between 179° and 180°. In solution it is not coloured by ferric chloride. It has the character of an organic acid, and displaces the carbonic anhydride in carbonates.

Silver dimethoxybenzote, $C_6H_3(OCH_3)_2.CO_2Ag$. — Dimethoxybenzoic acid was dissolved in ammonia, and the excess of ammonia driven off by warming. On adding silver nitrate, the salt separated out in slender white needles, which were obtained by recrystallisation from hot water in pure acicular tufts. They were sparingly soluble in cold, easily in hot water. Contained 37·63 per cent. of silver; theory gives 37·61 per cent.

By the oxidation of eugenol-ethyl-ether, which boils at 251° and not at 240° as stated by Cahours, a corresponding dimethoxybenzoic acid was obtained, which was not further investigated.

The behaviour of eugenol-methylether with chromic acid, confirms the formula of eugenol, $C_6H_3\left\{\begin{matrix}OH\\OCH_3\\C_3H_5\end{matrix}\right.$, founded by Cahours† on the formation of methyl iodide by heating with hydriodic acid, and of protocatechuic‡ acid by fusing with potassium hydrate.

The authors were not able to obtain an acid by the direct oxidation of eugenol, as it gave a brownish non-crystalline mass, which was not soluble in water, alcohol, benzene, or any other solvent, and from which no definite chemical compound could be obtained. On heating, car-

* Marasse (Ann. clii, 59) threw some doubt on the fact that the authors had obtained anisic acid by the oxidation of the methylether of cresol from tar. The authors, on repeating the research, observed a second acid present, together with anisic acid. Körner states that besides anisic acid, methoxybenzoic acid has been obtained from the above-mentioned methylether.

† Zeitschr. f. Chem. 1866, 466.

‡ Hlasiwetz and Grabowski, Ann. Ch. Pharm., cxxxix, 95.

bonic anhydride and water escaped, while the residue smouldered away on exposure to the air, and left pure chromic oxide.

E. T. C.

Note on the Researches on the Formation of Gallic Acid. By M. Sacc.*

It has generally been admitted, since the researches of Pelouze, that gallic acid has the formula $C_7H_3O_5HO$, and that it is derived from tannic acid by the splitting up of the latter, sugar at the same time being formed in the presence of water. Stenhouse, however, has long since shown that tannic acid gives an *equal* weight of gallic acid. Besides, when gall-nuts are fermented, neither carbonic anhydride nor alcohol is formed.

To clear up this question, the author exhausted 100 grm. of gall-nuts with ether, and obtained 43 grams of pure dry tannic acid. On the other hand, 500 grams of the same powder fermented for three months with 2 litres of water, produced 252 grams of pure dry gallic acid. Since, then, it appears from the above experiment that tannic acid increases in weight when changed into gallic acid, the author concludes that the change is nothing but a simple hydration, and that tannic acid is probably the anhydride of gallic acid.

E. T. C.

Researches on Valeraldehyde. By A. Schroeder. Part II.†

Valeraldine is obtained by passing dry ammonia over sulpho-valeraldehyde—

$$3C_5H_{10}S + 2NH_3 = C_{15}H_{31}NS_2 + NH_4SH.$$

Thus prepared it contains an excess of ammonia, which may be removed by a current of hydrogen, or by dissolving it in ether and evaporating the solution *in vacuo* over sulphuric acid. It is thus obtained as an oil, which, by standing over sulphuric acid *in vacuo* for some time, and then being exposed for a short time to the air, becomes crystalline. The oily valeraldine may also be solidified by passing hydrocyanic acid over it. It melts at 41°, and is a very indifferent body, not acted upon by hydrocyanic acid, cyanogen gas, or cyanogen chloride; it is insoluble in water, soluble in alcohol and ether; from the latter it crystallises in white leaves, resembling ferns, and having the consistence of wax. Its odour resembles that of acetamide. When heated, it distils with decomposition; *in vacuo* it sublimes without decomposition.

Carbovaleraldine is formed, either by shaking a mixture of carbon disulphide and valeraldehyde with aqueous ammonia, or by adding

* Compt. rend., lxxii, 766. † Deut. Chem. Ges. Ber., iv, 468—472.

carbon disulphide to an alcoholic solution of valeraldehyde ammonium—

$$2C_5H_{10}O + 2NH_3 + CS_2 = C_{11}H_{22}N_2S_2 + 2H_2O.$$

Its vapour density, determined in vapour of water and oil of turpentine, was found to be 60·08 and 60·4 instead of the calculated 120·3, showing that the compound already dissociates between 100° and 160°. It is insoluble in water, soluble in cold ether and alcohol, crystallising from the latter in small warty crystals. It melts at 115·5°—117°, and is decomposed on heating it above this temperature, but may be sublimed *in vacuo*.

Valeraldehyde-ammonium.—To obtain an insight in the constitution of this body, the vapour-density was determined at 160°, and found to be 52·16; calculated for 2 vols. 51·5. The vapour-density of the compound $C_5H_9(NH_4)O + 7H_2O$ was found to be 14·31, showing that the compound has also a normal density in presence of water for $14{\cdot}31 \times 16 = 228{\cdot}86$, the molecular weight of the compound; and subtracting the weight of the water, we have $228{\cdot}96 - 114 = 102{\cdot}96$, the molecular weight of the anhydrous compound, and $\frac{102{\cdot}96}{2}$ its vapour density.

Acetaldehyde-ammonium has also a normal vapour-density (at 100° = 30·33, and at 160°, 30·36, the calculated value being 30·5), but at 185° dissociation begins, as at that temperature the vapour-density was found to be 27·77.

If these compounds are regarded as aldehydes, in which one hydrogen is replaced by ammonium, it may be expected that ammonium chloride also will have a normal density between 185° and 300°.

These determinations were made by Hofmann's new method; that the presence of water has no disturbing influence was further shown by ascertaining the following vapour-densities:—

Acetchloralhydrate.	Found.	Calculated for 4 vol.
$C_2Cl_3HO.H_2O$	41·08	41·37
Terpin hydrate.		
$C_{10}H_{20}O_2.H_2O$	47·28	47·5

As these vapour-density determinations can be carried out so very easily, the author tried to determine by this method the water of crystallisation in different salts, and obtained the following results:—

	Calculated.	Found.
Sodium carbonate.....	62·93	62·58
Potassium alum	45·52	45·30
Magnesium sulphate.....	51·22	50·93
Potassium oxalate.....	9·78	9·62
Sodium potassium tartrate ..	25·53	25·41
Sodium phosphate	60·33	60·04

In salts which do not lose all the water at 185°, only that quantity which escapes at this temperature can be found by this method:—

	Calculated.		Found.
Copper sulphate	5 mol.	4 mol.	—
	36·13	28·91	28·73

The following determinations show that the density of bodies boiling at 270° can be determined in vapour of aniline, and that for those boiling not above 182° vapour of water can be used.

	Found.	Calc.
Coumarin, b. p. 270° ..	74·28	73·0
Aniline, b. p. 181°·5 ..	46·02 46·07	46·5

Another advantage of the new method is that very small quantities are sufficient for a determination, thus the quantities of aniline used in the above experiments were 0·0059 and 0·0122. In a third experiment 0·0189 were taken, but the quantity was too large to be completely volatilized.

C. S.

On Acridine. By Graebe and Caro.*

The authors succeeded in isolating a basic substance from crude anthracene, to which, on account of its irritating action on the skin and mucous membranes, they have given the name of acridine. The body is obtained by treating the semi-solid portion of coal-naphtha, which boils between 300° and 360°, with dilute sulphuric acid, and precipitating the acid solution with potassium dichromate. A dirty brown precipitate is obtained, which dissolves on repeated treatment with boiling water; the solution thus obtained yields, after filtration and cooling, orange-yellow crystals of the chromate of the base; these crystals, freed from the mother-liquor by washing, yield the free base when warmed with ammonia. Thus obtained the body is not quite pure, but it may be rendered so by recrystallising its hydrochloride. Acridine substance crystallises, as determined by Dr. P. Groth, in small four-sided, rectangular prisms of the rhombic system, whose edges are often but narrowly truncated by the vertical prism, while the ends are formed by obtuse domes.

Acridine melts at 107°, and distils without alteration at a temperature above 360°. It sublimes, even below its melting point, in large broad needles. It is almost insoluble in cold, and but little soluble in

* Ann. Ch. Pharm., clviii, 265—281.

boiling water; on the other hand, it dissolves readily in alcohol, ether, carbon bisulphide, and hydrocarbons. The dilute solutions show a beautiful blue colour by reflected light; it exerts a slight but distinct alkaline reaction on litmus.

When inhaled, either in dust or in vapour, it causes sneezing, and, in a large quantity, coughing; probably the irritating action of the higher fractions of coal-naphtha is attributable to acridine. Analysis of the body leads to the formula $C_{12}H_9N$, but a consideration of its salts and reactions indicates that this formula should be doubled. It is exceedingly stable; neither potassium hydrate, whether melted in an open vessel or heated to 280° with a small quantity of water, nor concentrated hydrochloric acid at the same temperature, alters the substance. It may be distilled unaltered over either ignited zinc or soda-lime. It is equally unattacked by oxidizing agents. It is most readily attacked by sodium-amalgam. Potassium dichromate and sulphuric acid convert it into a brownish-red substance, which does not yield any crystalline body. Ethyl iodide simply adds itself on to acridine, but without effecting a substitution.

The salts of acridine crystallise readily, but are not very stable, splitting up partially or wholly when boiled with water; thus the acetate is completely decomposed when its aqueous solution is evaporated, and even the sulphate and hydrochlorate are partially decomposed on boiling.

Acridine does not form a carbonate, and may be precipitated in the free state from solutions of its salts by sodium carbonate. There appear to be two series of salts, all of which are yellow.

Acridine sulphate, $C_{24}H_{18}N_2.H_2SO_4 + H_2O$, precipitated from a boiling solution of acridine in dilute sulphuric acid on cooling (the sulphuric acid not being in great excess). It forms golden-yellow needles, or by slow crystallisation, is obtained in tolerably large prismatic crystals; they effloresce over sulphuric acid, but still retain one molecule of water of crystallisation, which is not given up till the temperature is raised to 90° or 100°, and then acridine simultaneously sublimes. This salt is readily soluble in hot water, less so in cold, and very little soluble in alcohol.

Acid acridine sulphate, $(C_{24}H_{18}N_2)_2.3H_2SO_4$, is precipitated by alcohol from a strong sulphuric acid solution of the base in the form of yellow needles. It is readily soluble in water, and difficultly in alcohol; by recrystallisation from water it is converted into the neutral salt.

Acridine hydrochloride, $C_{24}H_{18}N_2,2HCl + 2H_2O$, is formed by direct combination of acridine with hydrochloric acid, the latter being in excess, and crystallises from water on cooling in brownish-yellow prismatic crystals, often several inches long. It must be washed with dilute hydrochloric acid, as it readily gives up hydrochloric acid to

water. It effloresces over sulphuric acid, and at the same time its brown yellow colour becomes pure yellow; the effloresced salt still contains two molecules of water, from which it cannot be freed without loss of hydrochloric acid. It also loses acid by long standing in the desiccator. It is readily soluble in water, but more easily in hot than in cold. Its solubility is decreased by the presence of hydrochloric acid, and it is difficultly soluble in alcohol.

Platinochloride of acridine, $C_{24}H_{18}N_2.2HCl.PtCl_4$, is precipitated from a solution of acridine in excess of hydrochloric acid by platinic chloride, as a yellow crystalline precipitate consisting of microscopic needles. The compound is scarcely soluble in water, and is gradually decomposed by boiling with water.—The *aurochloride*, $C_{24}H_{18}N_2.2HCl.2AuCl_3$, is prepared in a manner similar to that employed for the platinum compound.—The *mercuro-chloride*, $C_{24}H_{18}N_2.2HCl.HgCl_2$, prepared as the above described double salts, is a yellow crystalline precipitate.

Acid acridine chromate, $C_{24}H_{18}N_2.2CrO_4H_2$.—This is the compound employed in obtaining acridine; its preparation has been already described. It is soluble in a large volume of boiling water, but nearly insoluble in cold water. By recrystallisation from water which does not contain an excess of potassium dichromate, a chromous compound is obtained. When the dry salt is heated, the base volatilises unaltered, leaving chromic oxide.

Acridine nitrate is readily soluble in water, and crystallises in yellow needles.

Acridin periodide is obtained as a brownish-red crystalline precipitate by adding an alcoholic solution of iodine to a solution of the hydroiodide of the base. By repeated recrystallisation from hot alcohol the body $C_{24}H_{18}N_2.2HI.I_2$ is obtained pure. This substance forms brownish-red tables, which, by slow crystallisation, may be obtained very large, and then appear almost black. In powder it appears light brownish-red. It is easily soluble in hot alcohol, less so in cold. Water precipitates it from its alcoholic solution as a brown crystalline precipitate; the precipitate is slowly decomposed by boiling with water, iodine being liberated and acridine hydriodide passing into solution. The same decomposition is produced by treating the finely powdered salt with a solution of sulphurous acid. A compound containing even more iodine appears to exist.

Compounds of Acridine with Ethyl Iodide.—Two compounds are formed when these bodies are heated together; they are difficult to obtain pure, and the authors promise further observations concerning them.

Nitro-compounds of Acridine.—Acridine warmed with nitric acid of sp. gr. about 1·45, is readily attacked, and, according to circumstances, di- or tetranitro-substitution products are formed; the authors always obtained both products together. They are readily

separated, as the tetranitro-acridine does not unite with acids. On diluting the nitric acid employed in the nitration with water, the tetranitrated compound separates as an orange-red precipitate, while the dinitro-compounds, of which there are two, remain in solution; the last-mentioned bodies are therefore precipitated by ammonia, and separated by recrystallisation from alcohol. The least soluble.

α *Dinitroacridine*, $C_{24}H_{16}(NO_2)_2$, crystallises from alcohol in golden-yellow plates, which resemble chloranil; it melts at 214° and may be sublimed unaltered in plates. It is insoluble in water, slightly soluble in cold alcohol, rather more so in boiling alcohol, slightly in ether, and with moderate facility in chloroform. It forms salts with acids, which resemble the acridine salts, but in dilute solution they do not exhibit the beautiful blue fluorescence. The sulphate separates from a hot aqueous solution in golden-yellow crystals either acicular or prismatic; it is readily soluble in hot water, less so in cold water. The hydrochloride forms yellow prismatic crystals, easily soluble in water. The hydriodide is similar to the hydrochloride, and like acridine hydroiodide, forms a hyperiodide.

β *Dinitro-acridine* crystallises in hard plates or tables, frequently in warty masses, especially when not quite pure. In hot alcohol it is readily soluble, less so in cold alcohol and insoluble in water. It melts at 154°. With acids it forms salts which resemble those of the preceding body.

Tetranitro-acridine, $C_{24}H_{14}(NO_2)_4N_2$, obtained as above described, or in greater quantity by heating acridine with a mixture of sulphuric and nitric acids for some hours in the water-bath. On diluting the acids, the body precipitates. After washing with hot water and recrystallisation from glacial acetic acid, it is obtained in reddish-yellow tables. In alcohol, ether, and benzene, it dissolves with difficulty, more easily in boiling glacial acetic acid.

Hydro-acridine, $C_{24}H_{20}N_2$.—Obtained by the action of sodium amalgam on an aqueous or alcoholic solution of acridine; purified from acridine by treatment with acid and solution in alcohol, the latter dissolving the hydroacridine, and leaving a white body, which will be treated of below. Hydroacridine crystallises in colourless prisms, slightly soluble in cold alcohol, easily in hot alcohol and ether, insoluble in water. It melts at 169°, and may be sublimed in prismatic crystals; when further heated it distils, but not without decomposition. It is not attacked by dilute acids, dissolves in cold concentrated sulphuric acid, and is precipitated unaltered on the addition of water. If the sulphuric acid solution be heated to 100° and then diluted, no precipitation takes place, but a yellow solution is formed, from which ammonia precipitates acridine. When it is oxidized with dilute solution of potassium dichromate and sulphuric acid, acridine-

chromate is precipitated, and chromium sulphate remains in solution. Sodium amalgam converts the boiling alcoholic solution of hydroacridine for the most part into the above-mentioned white by-product, which the authors designate as *insoluble hydroacridine*. Hydroacridine treated with concentrated hydriodic acid yields a salt of acridine and a second base, which is either fluid or has a low melting point.

Insoluble Hydroacridine.—The authors have not succeeded in finally settling the formula of this substance, but have obtained numbers which indicate $C_{24}H_{22}N_2$ as its formula. This body is insoluble in alcohol, ether, benzene, carbon bisulphide, and chloroform; it is slowly dissolved by boiling nitrobenzene, but is, at the same time, converted into acridine. It dissolves in concentrated sulphuric acid when gently warmed with that substance, but is, at the same time, oxidized into acridine. On warming it sublimes, but the sublimate is soluble in alcohol, and consists of a mixture of acridine and hydroacridine.

E. T. C.

On Dinitro-aniline. By W. Rudnew.*

By the action of soda on dinitro-citraconanil, Gottlieb prepared a dinitro-aniline which crystallised in yellow tabular crystals, and melted at 185°; the author finds on repeating the experiment that this body melts at 175°, and is identical with the dinitro-aniline obtained by Clemm from chloro- and bromo-dinitro benzene (prepared either with dinitrophenol and phosphoric chloride, or by nitration of chloro- or bromo-benzene), and found by Clemm to crystallise in prisms and to melt at 175°; the same body is also produced by the action of strong alcoholic potash on dinitro-acetanilide prepared by the action of fuming nitric acid and oil of vitriol on acetanilide; this also melts at 175°. 1,000 parts of alcohol of 88 per cent. at 18° dissolve of these three products respectively, 5·4, 5·7, and 5·8 parts.

The dinitro-acetanilide used melted at 120°, mononitro-acetanilide melting at 207°; dinitro-citraconanil melts at 120°.

Nitrous acid does not act on dinitro-aniline suspended in nitric acid or in cold alcohol; when it is cautiously passed into a boiling mixture of the base and alcohol previously saturated with nitrous acid, a vigorous evolution of gas sets in, the whole becomes clear, and from the product water precipitates dinitro-benzene, melting at 87°, and identical with the previously known dinitro-benzene.

C. R. A. W.

* Zeitschr. f. Chem. [2], vii, 202.

On some Decompositions of Isomeric Bromotoluidines. By E. Wroblevsky.*

The author has previously found that the chlorotoluidine got by chlorinating paratoluidine, gives a diazo-compound, yielding by decomposition with alcohol, orthochlorotoluene; whilst by nitrating parachlorotoluene, two chlorotoluidines are obtainable whose diazo-derivatives treated with alcohol furnish two different methyl-chloro-phenetols. Bromotoluidines show analogous reactions; thus [the diazo-derivative of] orthobromo-metatoluidine decomposed by alcohol furnishes a bromocresol crystallising in yellow needles and melting at 88·5°; the potassium salt crystallises from water in beautiful red shining plates, and contains $C_7H_6Br_0(OK)_m + H_2O$; the diazo-derivative of orthobromo-paratoluidine similarly yields ortho-bromotoluene, boiling at 182° and yielding by oxidation with chromic acid solution, orthobromobenzoic acid melting at 153°; much resin is also found, but no trace of a cresol.

The diazo-derivative of orthobromo-metatoluidine treated with hydriodic acid, yields orthobromo-metaiodo-toluene, $C_7H_6Br_0I_m$, as a fluid not solidifying at −20°; B. P. 200; sp. gr. 2·139 at 18°; by nitration this yields nitro-orthobromo-metaiodotoluene, $C_7H_5(NO_2)Br_0I_m$, easily soluble in alcohol, crystallising therefrom in prismatic crystals, and melting at 86°.

C. R. A. W.

On the Derivatives of Phosphine corresponding to Ethylamine and Diethylamine. By A. W. Hofmann.†

In this notice Prof. Hofmann describes the preparation and properties of the primary and secondary phosphines in the ethyl series, which, after long-continued efforts, he has finally succeeded in obtaining.

The method pursued is to act on phosphonium iodide with the alcoholic iodide, in presence of a metallic oxide, such as zinc oxide; the ordinary zinc-white of commerce was found to answer all purposes. Numerous experiments showed the best proportions to be 1 mol. zinc oxide to 2 mols. phosphonium iodide and 2 mols. alcoholic iodide. In preparing the ethylphosphines, a mixture of one part by weight of zinc-white, four parts phosphonium iodide, and four parts ethyl iodide was digested in sealed tubes for 6 to 8 hours at a temperature not exceeding 150°; at the end of this time, the tubes were found to be filled with a homogeneous, almost colourless, crystalline mass. A tube of about 50 c.c. capacity may be charged with 40 to 45 grams of the mixture. In filling the tubes, it is expedient first to introduce the phosphonium iodide, then the zinc oxide, and, finally, the ethyl iodide; thus ar-

* Zeitschr. f. Chem. [2], vii, 240. † Deut. Chem. Ges. Ber., iv, 430.

ranged, these bodies do not react at ordinary temperatures, and the tubes may be sealed with safety.

The main product of the reaction is *ethylphosphonium iodide*, which unites with the zinc iodide to form a double salt :—

$$2C_2H_5I + 2(H_3P.HI) + ZnO = 2(C_2H_5H_2P.HI) + ZnI_2 + H_2O.$$

Simultaneously, however, reaction takes place, but to a less extent, between 2 mols. ethyl iodide, 1 mol. phosphonium iodide, and 1 mol. zinc oxide :

$$2C_2H_5I + H_3PHI + ZnO = (C_2H_5)_2HP.ZnI_2 + H_2O + HI$$

with formation of *diethylphosphine*, which combines directly with the zinc iodide. A small quantity of phosphonium iodide, therefore, always remains unacted upon. Together with these reactions, others take place, especially when the temperature has risen at all high, which give rise to the formation of permanent gases, perhaps ethylene or even marsh-gas. In these cases the product is no longer pure white, but has more or less of a reddish-yellow colour, in consequence of the separation of phosphorus iodide ; the escaping gases then take fire only momentarily, whereas, when phosphine is present, they burn for some minutes.

It is worthy of note that the reaction described gives rise to the primary and secondary phosphines *only*, and since, as far as has been observed, the same appears to hold good in the methyl series, the reaction of phosphonium iodide on the iodides of the radicals is complementary to its action on the alcohols, in which case, as has been previously shown by the author,* the tertiary and quaternary bodies only are formed.

The separation and purification of the two phosphines present in the product of the reaction is accomplished without the least difficulty, and is based on the fact that the salts of the primary phosphines are perfectly decomposed by water, in the same manner as phosphonium iodide, with liberation of the phosphine and solution of the acid ; whereas, the salts of the secondary phosphines withstand the action of even a large excess of boiling water, but are readily decomposed by alkalies. The operation is as follows :—The product from several tubes being placed in a suitable apparatus, from which the air is expelled by a current of hydrogen, is acted on by a slow stream of water, which has been previously boiled and again cooled ; the monethylphosphine is thus set free and condensed in a spiral surrounded by ice. As some quantity of the extremely volatile phosphine is liable to be carried away by the hydrogen, the gas is caused to pass, before its entry into the atmosphere, through a column of concentrated hydriodic

* P. 407 of this volume.

acid. During the operation this liquid becomes gradually filled with magnificent, dazzling white crystals of pure ethyl-phosphonium iodide. When, by the further addition of water, even on warming, no more monethylphosphine is evolved, strong caustic soda-solution is added, the operation being still carried on in a current of hydrogen. The diethylphosphine then distils over readily on heating, and may be condensed in the ordinary manner. The liquid thus obtained, after drying over potassic hydrate, is the chemically pure diethylphosphine.

Monethylphosphine $P\left\{\begin{matrix} C_2H_5 \\ H \\ H \end{matrix}\right.$. Mobile, colourless, transparent liquid, boiling at 25°; lighter than, and insoluble in water; refracting light strongly, and entirely without action on vegetable colouring matters. It possesses a most overpowering odour, resembling that of the formonitriles; and, similarly, its vapour produces on the tongue an intensely bitter taste which extends far down the throat. Its fumes bleach cork, like chlorine; caoutchouc is affected by it in a remarkable manner, becoming transparent and losing its elasticity. In contact with chlorine, bromine, or fuming nitric acid, it takes fire; sulphur and carbon bisulphide combine directly with it, but the resulting bodies are liquid, and not crystalline like the corresponding triethylphosphine derivatives. Concentrated hydrochloric, hydrobromic, and hydriodic acid unite with it to form salts; the solution of the hydrochloride yields with platinum tetrachloride a double salt, crystallising in magnificent carmine-red needles, much resembling chromic anhydride when freshly prepared. The *hydriodide*, $C_2H_5H_2P,HI$, forms white quadrilateral plates, which may be sublimed unchanged in a current of hydrogen at the temperature of boiling water; the crystals are permanent in dry air; it dissolves in water with complete decomposition; also in alcohol, but with partial decomposition; in ether it is insoluble; concentrated hydriodic acid is the only solvent which dissolves it, though sparingly, unchanged; the addition of ether causing the separation of the salt in large, well formed plates, often a centimetre in diameter, but of extreme thinness.

Diethylphosphine $P\left\{\begin{matrix} C_2H_5 \\ C_2H_5 \\ H \end{matrix}\right.$. Colourless, transparent, perfectly neutral liquid, refracting light strongly, insoluble in water and lighter than it. It boils constantly at 85°, or 60° higher than the primary base. It has a penetrating, persistent odour, different from that of monethylphosphine, more resembling, although essentially different from that of triethylphosphine. It absorbs oxygen with great avidity, combination taking place with such energy as often to cause the mass to take fire when the containing vessel is opened. Diethylphosphine combines both with sulphur and with carbon bisulphide to form liquids, a

behaviour which enables the absence of triethylphosphine in it to be readily determined. It is easily soluble in all acids, but, with the exception of the hydriodide, all the salts seem difficultly crystallisable. The hydrochloride yields with platinum tetrachloride a readily alterable double salt, crystallising in fine, large, orange-yellow prisms. The salts of diethylphosphine are not decomposed by water.

This discovery of ethyl- and diethylphosphine renders the parallelism between the two series of derivatives of ammonia and phosphine perfect, as will be evident from the following:—

Ammonium iodide.		Phosphonium iodide.
H_4NI ..		H_4PI
$C_2H_5\ H_3NI$ ..	Primary substitution ..	$C_2H_5\ H_3PI$
$(C_2H_5)_2H_2NI$ ..	Secondary ,, ..	$(C_2H_5)_2H_2PI$
$(C_2H_5)_3H\ NI$ ..	Tertiary ,, ..	$(C_2H_5)_3H\ PI$
$(C_2H_3)_4\ NI$ ..	Quarternary ,, ..	$(C_2H_5)_4\ PI$

In conclusion, Prof. Hofmann anticipates the formation of bodies in the phosphorus series corresponding to the amides, nitriles, and formonitriles, and of phosphorised mustard oils. Possibly also the method described may lead to the discovery of the still missing monarsines and monostibines. H. E. A.

On Biuret. By H. Huppert and J. Dogiel.*

The authors found some years ago that allophanic ether can easily be transformed into biuret. As Hofmann has lately effected the same synthesis by another method, the authors now publish the details of their reaction, which consists in heating thin layers of allophanic ether in an atmosphere of ammonia; the reaction commences at 200°, when alcohol begins to distil over. The residue is a very impure biuret, and the yield is small, because a portion of the ether sublimes, and because the temperature at which biuret decomposes is about the same as its melting point (190°), which is lower than that of allophanic ether. Consequently a great part of the biuret formed is already decomposed before all the ether is acted upon. C. S.

On a New Base from Extract of Meat. By G. H. Weidel.†

The well-known nutritive properties of meat-extract, and especially its remarkable powers as "Genussmittel"‡ lead naturally to the sup-

* Deut. Chem. Ges. Ber., iv, 475—476. † Ann. Ch. Pharm., clviii, 353—369.

‡ "Genussmittel," a substance which, by its presence, aids the assimilation of other nutritive bodies; is labour-saving, and, in a certain sense, strength-enhancing (Liebig); which does not give actual strength, only the sensation of vigour, by a peculiar action on the nervous system. (Voit.)

position that creatine and creatinine are the substances that give it these powers; Voit, however, having maintained that this action of meat-extract does not arise from the presence of these bodies, experiments on large quantities of extract were made, which resulted in the discovery of a new base, *carnine*, $C_7H_8N_4O_3$, constituting about 1 per cent. of the extract, which was furnished by Liebig for this purpose.

The extract is dissolved in 6 or 7 parts of warm water, and carefully precipitated with strong baryta-solution, avoiding excess: the mass is filtered through a linen cloth; and the filtrate precipitated by basic lead acetate. A lead-compound of carnine is thus thrown down (*inter alia*), and being soluble in boiling water, can thus be separated from the other bodies likewise precipitated. The aqueous solution thus obtained is decomposed while boiling with hydrogen sulphide, and the filtrate from the lead sulphide is evaporated to a small bulk and separated from a crystalline mud sometimes deposited on standing, and due to the presence of variable quantities of sodium chloride in the extract employed, whereby ultimately more or less hydrochloric acid is found in the crude carnine solution: the liquid portion is precipitated by strong solution of silver nitrate, and from the mixed silver chloride and silver-compound of carnine thus produced, the former is dissolved out by diluted ammonia solution, the latter being almost insoluble in this medium: finally, the silver compound is washed with boiling water, decomposed by hydrogen sulphide, and the filtrate decolorised with animal charcoal, a considerable portion of carnine being, however, absorbed by the charcoal. From the colourless aqueous solution thus obtained, carnine crystallises on cooling in chalk-white druses and friable groups of extremely small irregular crystals. The analytical numbers agree well with the formula $C_7H_8N_4O_3$ after drying at 100°, one molecule of water of crystallisation being present in the air-dried substance.

The hydrochloride is obtainable in needles on cooling the hot solution of carnine in strong hydrochloric acid; these needles, freed from the mother-liquor and redissolved, do not again make their appearance, a mud separating, which however on standing, again becomes perfectly converted into needles; the salt is anhydrous. Both the hydrochloride and the platinum-salt gave satisfactory numbers on analysis.

Silver nitrate throws down from a carnine solution a flocculent white precipitate, which is insoluble in nitric acid, and also in ammonia; dried at 100° it has the composition $2(C_7H_7AgN_4O_3) + AgNO_3$; theobromine, which differs from carnine by only one oxygen-atom, does not yield an analogous body, the silver compound being $C_7H_7AgNO_2$; sarcine on the other hand yields the compound $C_5H_4N_4O + AgNO_3$.

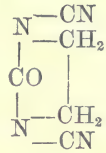
Concentrated hydriodic acid does not reduce carnine to theobromine;

neither does long boiling with baryta-water produce any change (no ammonia or methylamine is evolved, and unaltered carnine is found after precipitating the baryta with carbonic acid).

Bromine-water in slight excess on the water-bath, gives a slight evolution of gas; after evaporation, crystals of the hydrobromide of sarcine separate, from which alkalies precipitate the base itself, soluble in excess, but nearly insoluble in cold water. From analyses of the base and its hydrobromide, and from its properties, it appears to be identical with Strecker's sarcine, the only observed difference being that whereas Strecker states that his body is not precipitated by lead acetate, the one thus obtained is precipitable by basic lead-acetate, but not by neutral lead-acetate, nor even by the basic lead salt in presence of the neutral one; Städeler also has prepared sarcine from the basic lead precipitate from flesh, liver, &c., &c.

Ordinary nitric acid gives a violent action on heating, from the product of which the nitrate of sarcine is obtainable on cooling: oxalic acid and an indistinctly crystalline yellow body are also produced.

Sarcine being considered as a urea derivative



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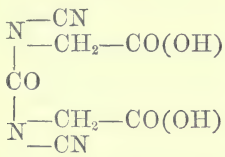
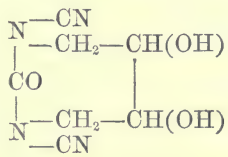
carnine may be regarded as either—



or,



and the production of sarcine from carnine by bromine appears to be in accordance with the equation—

$$C_7H_5N_4O_3 + 2Br = C_5H_1N_4O.HBr + CH_3Br + CO_2.$$

Bromacetic acid might possibly be formed; but this body was not distinguishable in the ethereal extract obtained with the product of the action of bromine.

Heated with fresh chlorine-water and a trace of nitric acid, evaporated on the water-bath to dryness, and placed in an ammoniacal atmosphere, a dark rose-red tint is produced with sarcine; carnine gives the same reaction, sarcine being previously formed.

The barium precipitate obtained in the method of extracting carnine above described is principally phosphate and sulphate; the portion of the lead precipitate insoluble in water contains inosite, a little lactic

acid, and some *succinic acid* (unknown before); and especially an amorphous extractive matter, part of which only is soluble in alcohol. The filtrate from the original lead precipitate yields, when evaporated, a crystalline lead lactate, and the filtrate from this when evaporated yields much creatine with a little creatinine, the mother-liquor of which contains considerable quantities of glutinous and dextrin-like substances.

Doses of $\frac{1}{2}$ to 2 decigrams of carnine and its hydrochloride appear to have a slight effect on the nervous system, a slackening of pulsation being the most marked symptom.

C. R. A. W.

On a New Blue Colouring Matter derived from Eserine. By A. PETIT.*

ESERINE, first exactly neutralised with dilute sulphuric acid, then treated with excess of ammonia and evaporated to dryness in a water-bath, yields a residue of a magnificent blue colour, soluble in water and alcohol, and crystallising in the form of elongated prisms. This residue stains the skin, nails, &c., and strongly dyes silk blue without the aid of a mordant; it changes by acids to a fine violet purple.

Eserine treated with ammonia, without previous saturation with sulphuric acid, yields on evaporation a greenish residue much less soluble, and turned red by acids.

J. B.

Leucine from Vegetable Proteides. By H. RITTHAUSEN and U. KREUSLER.†

1. *Preparation and Composition of the Leucine.*—The authors state that the leucine employed in this research was obtained by boiling the proteides with dilute sulphuric acid, and as a by-product in the preparation of glutamic and aspartic acids. It was obtained usually in indefinite plate-like lumpy masses, or sometimes in thick transparent nodules. It was always very impure, and contained, even after many washings with cold water, besides the constituents of the mother-liquor, tyrosine, amic acids, a sulphuretted compound, and bodies whose composition was expressed approximately by the formula $C_4H_7NO_2$. On purification by recrystallising from alcohol of sp. gr. ·89 to ·90, treatment with carbonate of barium, and decolorisation with pure animal charcoal, the leucine was obtained in thin, transparent, glistening plates. Combustions were made of six samples of leucine from various substances, and variously purified. The percentage of carbon obtained varied from 52·89 to 53·62, those of hydrogen from

* Compt. rend., lxxii, 569. † J. pr. Chem. [2], iii, 307—313.

9·63 to 9·96. One estimation of nitrogen was made, giving 10·43 per cent.

The formula of leucine, $C_6H_{13}NO_2$, requires 54·96 per cent. C., 9·22 H., 10·69 N., and 24·43 O.

As all the preparations contained a small trace of sulphur, some of the leucine was purified by treating it with potash, oxide of lead, and sulphuric acid. This sample gave 54·07 per cent. C., 10·13 H., 10·24 N., and 25·56 Cl.

These numbers show that though it is difficult to obtain pure leucine from vegetable proteides, still a body is obtained not differing from the leucine prepared from similar animal substances. The authors state unhesitatingly that all vegetable albuminous substances yield leucine, but the quantity obtained varies, as gummy protein substances and conglutin gave less than legumin; further, that it is difficult to estimate the quantity of leucine formed, since weighings of the impure leucine are untrustworthy, whilst so much is lost in purification that but little information is gained by weighing the purified substance. The quantity obtained from various substances was estimated roughly at 4 to 12 per cent.

2. *Combustion of the Leucine with Soda-Lime.*—The authors burnt the leucine with soda-lime alone, but could not get all the nitrogen off as ammonia; thus with four variously purified samples of leucine they obtained 6·76 per cent., 6·67 per cent., 7·14 per cent., and 7·9 per cent., instead of 10·69 per cent. as required by theory. They then mixed the substance with pure cane sugar and 40 times its weight of soda-lime, and they obtained from two of the same samples of leucine 10·43 per cent. and 10·24 per cent. The authors quote the case of a leucine-copper-compound which without sugar gave 5 per cent., with sugar, 8·29 per cent. N.

3. *Behaviour of Leucine with the Nitrates of Mercury.*—According to Erlenmeyer and Schöffer, Zollikofer, Gössmann, and Städeler, leucine in aqueous solution is not precipitated by mercury nitrates, whilst according to R. Hofmann it gives a white flocculent precipitate. With a solution of the purified leucine the authors found that neither the nitrates of mercury nor Millon's reagent produced the slightest turbidity. On the other hand the impure leucine, according to its greater or lesser degree of impurity, gave, under similar circumstances, a greater or lesser precipitate. The cause of this precipitate is the presence of a trace of amic (glutamic or aspartic) acids. As soon as these acids are removed, no precipitate is formed in the leucine solution by the addition of the mercury salt, so that the authors propose this negative result as a test for the purity of the leucine obtained.

4. *Compound of Leucine with Cupric Oxide.*—When a very dilute solution of leucine is boiled for some time with excess of hydrate of

copper, a portion of the latter dissolves to a blue liquid, and on cooling and evaporation, the compound separates in pure violet-blue glistening scales. It is very sparingly soluble in water, 2,517 parts of cold water dissolving 1 part. Three analyses led to the formula $3C_6H_{13}NO_2.2CuO$. A compound obtained by Kohler (Ann. Chem. Pharm. 134, 367) by boiling solution of leucine with acetate of copper was investigated. It formed suddenly in clear blue glistening plates. Four estimations of copper suggested the formula $7C_6H_{13}NO_2.4CuO$. E. T. C.

On the Occurrence of Aspartic and Glutamic Acids among the Decomposition-products of Proteides. By H. RITTHAUSEN and U. KREUSLER.*

a. From Vegetable Proteides.—The authors found that aspartic acid, $C_4H_7NO_4$, and glutamic acid, $C_5H_9NO_4$, are always produced, along with tyrosine and leucine, on boiling vegetable albuminous substances with dilute sulphuric acid. The substances which they investigated were legumin from peas, hog-beans, and oats. Gluten-casein from wheat-gluten, conglutin from lupines and almonds, maize-fibrin, mucedin, and a mixture of vegetable gelatin, mucedin and gluten-fibrin from wheat-gluten.

The relative quantities of the two acids produced by the various bodies differed so remarkably that the authors were induced to draw special attention to this point. The proteides of wheat-gluten, gluten-casein included, also maize-fibrin and conglutin from lupines and almonds, produce glutamic acid in quantity sufficient to crystallise out of the concentrated mother-liquor on standing for a few days, whilst the quantity of aspartic acid obtained is much smaller. Legumin from pulse on the contrary gives but little glutamic acid, but a larger quantity of aspartic acid. The following table gives the roughly estimated quantities by weight of the two acids obtained from various substances:—

	Aspartic acid.	Glutamic acid.
1. Mucedin	Not estimated.	25 per cent.
2. Maize-fibrin	1·4 per cent.	10·0 ,,
3. Mixture of vegetable gelatin, mucedin, and fibrin	1·1 ,,	8·8 ,,
4. Gluten-casein	0·33 ,,	5·3 ,,
5. Conglutin (from lupins)	2·0 ,,	3 to 5 ,,
6. Legumin (from hog-beans)	3·5 ,,	1·5 ,,

The numbers in experiments 1 to 5 under "Glutamic acid" give the quantity which crystallised out of the mother-liquor, and was purified

* J. pr. Chem. [2], iii, 314—317.

by solution in water. In experiment 6, the glutamic acid adhering to the aspartic acid was also extracted. When the quantity of aspartic acid was small it was estimated as the copper salt.

The differences of yield shown in the foregoing table, especially in the quantity of glutamic acid, prove that the original protein bodies differ from each other. The authors state that wheat-gluten is the most suitable substance for the preparation of glutamic acid, the acid being obtained well crystallised and quite pure. Conglutin is also suitable, and at the same time yields a considerable quantity of aspartic acid.

b. From Animal Proteides.—From the published researches of Kreusler (J. pr. Chem. cvii, 240—245) it appears that egg albumin, casein, and horn, when boiled with sulphuric acid, form aspartic acid (besides tyrosine and leucine), but no glutamic acid. The authors, however, state that as glutamic acid is with difficulty obtained pure and crystallised, even as a copper salt, it might easily be overlooked if present only in small quantity. Aspartic acid is shown by these researches to be one of the decomposition-products of all protein substances, and takes its place by the side of tyrosine and leucine.

E. T. C.

On Paralbumin. By P. Plósz.*

This memoir is directed to an investigation of the substance which Hoppe-Seyler found to be associated with albumin to form the body described by Scherer as paralbumin.

The albumin contained in cystic fluids has hitherto been but little investigated, and it is not known whether it is composed of one or of several albuminous bodies. The albumin is held in solution by alkali, from which it is precipitated by much water and carbonic acid, or by very dilute acetic acid. By alcohol it is precipitated together with a portion of the alkali; and after long standing under alcohol, it is redissolved by moderately warm water. On boiling a cystic fluid, a portion of the albumin is coagulated; but if the liquid be neutralised before boiling, the whole of the albumin is coagulated. Dilute hydrochloric and sulphuric acids convert it into syntonin, which can then be precipitated by sodium sulphate or chloride. The reducing body remains in solution when either method of precipitation is employed; hence this peculiarity of the substance permits of its ready separation from albuminous matters.

One method of producing the substance is as follows:—The liquid is carefully neutralised with dilute acetic acid, and precipitated with thrice its volume of alcohol. The precipitate is washed with alcohol,

* Med. Chem. Unters., 1871, 517.

on a filter, pressed, mixed with water, and heated to the boiling point. The solution filtered off from the coagulated albumin is kept exactly neutral, concentrated to a small bulk, and precipitated with alcohol. The precipitate, after being well washed with water, contains the substance free from albumin. In order to purify it still further, it is again dissolved in water, heated to the boiling point, filtered, and again precipitated and washed with alcohol.

Another method was followed with a second cystic fluid. This was mixed with an equal volume of a saturated solution of sodium chloride and so much hydrochloric acid, that one gram of hydrogen chloride was contained in 100 c.c. In this manner the albuminous body was very completely precipitated after being changed into syntonin. The fluid was separated from the precipitate by straining and filtration, lastly neutralised, and evaporated to a small bulk, then filtered from the sodium chloride, which had separated, and from some albumin; next precipitated by a large quantity of alcohol, and washed. Lastly, the substance was redissolved in water, warmed, filtered, and reprecipitated by alcohol.

As thus prepared, the substance contains a considerable quantity of sodium chloride, from which it can be freed only by prolonged washing with alcohol. By the other method, however, of precipitating the albuminous body by alcohol and heat, the fluid is separated from the precipitate with difficulty, and there is danger that by prolonged contact with water decomposition may ensue. The substance thus obtained is, when moist, white, gelatinous, and very like syntonin. It is soluble in water, and separates therefrom on concentration, in the form of a skin, which, when dried, is of a dirty grey colour, like a dried brittle mass of albumin. When once dried, it no longer dissolves to form a clear solution. Its aqueous solution is opalescent, but can be rendered transparent by repeated filtration; but it again becomes turbid on standing. The body is precipitated from its solution by alcohol, mercuric chloride, and mercuric nitrate; but it is not precipitated by strong or dilute acids, cupric sulphate, or potassium ferrocyanide. The aqueous solution dissolves cupric hydrate on boiling, without the addition of an acid, but does not reduce the oxide. It is not coloured by iodine.

On boiling its clear solution with mineral acids, a flocculent, dirty brown precipitate is produced. On filtering off this precipitate, the filtrate, after neutralisation, is no longer precipitable by alcohol; it reduces cupric hydrate in alkaline solution, before the boiling point is reached; bismuth oxide, and indigo on boiling; and is turned brown when boiled with caustic potash. In aqueous solution this substance is decomposed on heating, as well as when boiled with acids, and then yields to alcohol considerable quantities of the reducing body.

The precipitate formed by this decomposition is insoluble in water, alcohol, and acids: soluble in alkalies. It gives none of the reactions for albumin (formation of xanthoproteic acid on heating with strong nitric acid, violet coloration with cupric oxide, &c.).

Neither before nor after heating did the watery solution of the body exhibit any action on polarized light. The aqueous solution of the product of decomposition acts as a most energetic reducing agent, even when extremely dilute.

Analysis of the original substance gave the following numbers:—C. 49·7; H. 7·6; N. 7·4—8·8 per cent. The variable percentage of nitrogen is accounted for by the readiness with which the body is decomposed; and hence the varying quantities of the reducing body which it contains. This latter is probably a kind of sugar, and consequently the original substance is a glucoside. Its likeness to mucin demands further investigation. From the original substance a nitro-compound has been prepared by the author.

T. S.

Solubility of Gelatin in Glycerin. By R. FRESENIUS.*

AT ordinary temperatures, gelatin is slightly soluble in, and slowly permeated by glycerin. It does not swell in glycerin as it does in water. It is completely dissolved by long digestion in glycerin, a little below 100°, forming a solution which gelatinises on cooling. Gelatin which has been well soaked in water dissolves about as easily in hot glycerin as in cold water.

A. T.

Contributions to the Chemical Knowledge of Ergot. By J. C. HERRMANN.†

ON thoroughly exhausting 20 ounces of finely powdered ergot with ether, there were ultimately obtained 6 ounces of a fatty oil, which, when saponified with soda-ley, yielded a distillate containing ammonia, trimethylamine, and a liquid from which common salt separated a soap, the aqueous portion containing glycerin; this soap treated with sulphuric acid yielded a semi-solid oil, the aqueous liquor from this operation yielding traces of butyric and acetic acids on distillation. By pressure in bibulous paper, a solid fat was obtained from this semi-solid oil; and after several recrystallisations from alcohol, this fat was found to melt constantly at 62°, and to solidify at 57°—58°, and gave numbers agreeing with those required for palmitic acid. From the fact that the oil was not a drying oil, and from the behaviour of the fluid portion with nitric acid (elaidic acid was produced), it was inferred that oleic acid was also present.

* N. Repert. Pharm., 232. † N. Rep. Pharm., xx, 283—301.

From an alcoholic solution of the mixed fatty acids, acetate of lead threw down a precipitate having the composition:

$$[C_{32}H_{31}(2PbO)O_3] + 3[C_{36}H_{33}(PbO)O_3]^*$$

and this, when treated with ether, yielded an insoluble portion having the composition:

$$5[C_{32}H_{31}(2PbO)O_3] + 4PbO]$$

(a basic palmitate), and a soluble portion of composition—

$$5[C_{36}H_{33}(PbO)O_3] + 4C_{36}H_{34}O_4$$

(an acid oleate).

By treating a portion of the extracted oil with alcoholic ammonia, separating the alcoholic liquor from the oily portion, and evaporating, a dark-brown aromatic-smelling residue was obtained, agreeing in properties (saving its solubility in ether) with the ergotine of Wiggers.

Contrary to the statements of Manassewitz, the oil was found to be saponifiable with caustic potash, the soap being softer than that obtained with soda.

By exhausting ergot with water, precipitating with lead acetate, and treating the filtrate with mercuric chloride, a precipitate was obtained from which the ecboline of Wenzell was separated, either by treatment with lead oxide or basic lead carbonate, or by Wenzell's process, viz., treatment with hydrogen sulphide, and then successively with freshly-precipitated silver phosphate, milk of lime, and ammonia carbonate. The product, freed by heat from excess of ammonia carbonate, had an alkaline reaction, and gave white precipitates with mercury chloride, tannic acid, and potassium cyanide; yellow with phosphomolybdic acid, orange with platinic chloride, red-brown with potassium biniodide (*sic*), and brownish with gold chloride.

The ashes of ergot were found to have the following composition:—

NaCl.	K_2O.	Na_2O.	CaO.	MgO.	Al_2O_3.	Fe_2O_3.	MnO.	P_2O_5.	SiO_2.	
1·51	30·06	0·65	1·38	4·88	0·59	0·86	0·26	45·12	14·67	= 99·98

C. R. A. W.

* H = 1; O = 8; C = 6; Pb = 103·5.

Researches on the Constituents of Ergot. By J. B. GANSER.*

BY extraction with ether, finely-powdered ergot yields 30 per cent. of its weight of fatty oil, containing a resin separable from the fats by nearly absolute alcohol, and giving to them a peculiar bitter rough taste and brownish tint. With lead oxide a plaster is obtained with these fats, from which ether extracts lead oleate; with soda-ley of 1·3 sp. gr., a soap is obtained; no free ammonia distils over during the operation, the distillate being neutral; on the addition of hydrochloric acid, however, thick white clouds are formed, and the colourless distillate becomes reddish.

The oil readily yields elaidic acid with nitric acid; a dose of 10 grams, given in two portions of 6 and 4 grams each, only produced a sensation of nausea, without actual vomiting; the last 4 grams increased the pulse and produced a slight faintness and perspiration, all symptoms ceasing in five hours. The oil extracted with alcohol yielded a resin and a small quantity of crystals, giving the cholesterin reactions; this resin possesses the same physiological properties as the oil, but in a much more marked degree.

Pulverised ergot heated, *per se*, in a water-bath in a retort, gave no volatile bases; and the same was found on heating 250 grams of ergot with 150 of $CaCO_3$ and 500 of water; but the residue from the ether extraction of the fatty acids had a strong smell of herring-brine (propylamine), and on distillation with oxalic ether, yielded a distillate containing ammonia, and giving the smell of animal oils; the residue in the retort from this operation, distilled with water, gave ammonia and a smell of animal oils. Hence neither ammonia nor trimethylamine pre-exists in ergot, but these bodies are formed only by decomposition of other substances contained by the reagents employed.

By boiling with water the residue left after extraction of ergot with ether, precipitation with lead acetate, and of the filtrate from this with mercury chloride, a precipitate is obtained which, when treated successively with freshly-precipitated silver phosphate, milk of lime, and carbonic acid, yields finally, after evaporation, a brown, hygroscopic, amorphous powder of ecboline; this is soluble in water and alcohol, insoluble in ether and chloroform; on boiling it with potash, ammonia is evolved; it has a bitter taste with sweet after-taste, and, in small doses, produces nausea and vomiting. The filtrate from the mercury precipitate of ecboline, on precipitation with phosphomolybdic acid and digestion of the precipitate with $BaCO_3$, and evaporation, furnishes ergotine as a greenish-yellow, glistening, amorphous, hygroscopic powder: it forms deliquescent salts, the hydrochloride crystallising in

* N. Rep. Pharm., xx. 301—315.

long slender needles; given to a young dog in small doses, it produces symptoms of nausea, without actual vomiting.

On distilling with sulphuric acid the aqueous extract from the ergot deprived of fats by ether, an acid of peculiar odour was obtained, which reduced silver nitrate (ergotic acid); on distilling with alcohol and sulphuric acid, formic ether was found in the distillate.

On extracting with alcohol of 80 per cent. the residue deprived of fats by ether, a cherry-red tincture is obtained, which deposits flocks of a sugar which reduces potassic copper solution (identical with mycose?).

3·2 per cent. of albumin was found in the infusion of ergot, also potash, lime, and magnesia, with hydrochloric, sulphuric, and phosphoric acids.

C. R. A. W.

On Persea gratissima Gærtner (Lauraceæ). By T. PECKOLT.*

PECKOLT has examined the fruit of this tree, which is also known as *Laurus Persea* (Linn.). He finds that 100 parts of the fresh rind, kernel, and pulp, contain respectively—

Rind—

Water	78·470
Fat containing chlorophyll	1·165
Light brown resin	1·300
Albumin, Sugar (traces), Tannic acid, Extract and cellulose	19·065

Kernel—

Water	58·876
Fatty oil	0·129
Grape-sugar	1·081
Starch	8·534
Albumin	1·301
Tannic and gallic acids	1·572
Red colouring matter, Succinic acid (traces), Gum, inorganic salts	4·420
Cellulose	26·087

* Arch. Pharm. [2], cxlvi, 114.

Fresh Pulp—

Water		80·670
Light yellow fatty oil		8·500
Grape-sugar		3·175
Starch		1·877
Malic acid	combined with calcium and potassium.	0·043
Tartaric acid	combined with calcium and potassium.	0·082
Albumin		0·075
Glutinous substance		1·559
Dextrin, mucus, &c.		2·775
Cellulose		1·244
Ash		0·982

100 parts of the dried pulp contain 5·109 parts of ash and 1·353 part of nitrogen.

From the analysis of the rind it will be seen that it can be used for fodder; the dried kernels would also form a good source of nourishment for animals. The pulp is eaten in Mexico with salt, and in the Antilles a vegetable soup is made from it. It has a sweetish taste, and can be eaten as cream with lime-juice, wine, and sugar.

The leaves, flowers, and pulp of this tree have been used in medicine. A. P.

Physiological Chemistry.

On the Metamorphosis of Albuminous Substances in the Bodies of Ruminants. By STOHMANN, R. FRÜHLING, and A. ROST.*

STOHMANN communicates the following as the chief results of his experiments:—1. The whole of the albuminoïds undergoing decomposition in the organism, appear in the form of oxidation-products in the solid and liquid excretions. These results were obtained with food not only poor, but also rich in nitrogen.

2. The metamorphosis of albumin is dependent on the quantity of albumin in circulation in the organism. As a rule, the metamorphosis of albumin rises and falls with the albumin in the food. The increase of albuminous matters above a certain quantity is a waste with adult animals.

3. The imbibition of large quantities of water increases the metamorphosis of nitrogenous matters. A goat, fed on 700 grams of hay and 800 grams of linseed-meal, took on four successive days 6,151, 3,600, 3,650, and 3,275 grams of water, and excreted in the urine

* Chem. Centr., 1871, 377.

33·10, 29·34, 28·69, and 27·52 grams of nitrogen, whilst during preceding experiments the average daily secretion of nitrogen was 28·9 grams.

4. The excretion of nitrogen quickly adapts itself to an increase of nitrogen in the food.

5. With an insufficiency of albumin in the food, the body becomes poorer in albumin. A goat, which daily consumed in its food 8·27 grams of nitrogen, excreted 11·1 grams. The 2·53 grams lost daily correspond to 74 grams of flesh. The weight of the animal sank in the ten days of the experiment from 31·54 to 29·72 kilograms.

6. Considerable increase of weight took place when, along with a sufficiency of albumin, larger quantities of non-nitrogenous substances were administered.

These experiments show that the metamorphosis of nitrogenous nutritive materials takes place in the herbivora exactly according to the same law as Voit has established for the carnivora, and that relative to the metamorphosis of albuminous matters, there is no distinction between carnivorous and herbivorous animals, save that the nitrogenous products of decomposition assume a different form, so that in the herbivora a portion of the nitrogen takes the form of hippuric acid, a substance which is wanting in the carnivora.

T. S.

Experiments on the Change of Material in the Adult Sheep under Uniform Feeding (Beharrungsfutter). By W. Henneberg, L. Schulze, M. Märker, and L. Busse.*

These experiments were carried out on two 4—5 year-old wethers. These animals were fed on so much meadow hay as was needed to keep them in *statu quo* as regards nourishment; each had also 6 grams of common salt daily, and water *ad libitum*. The animals lived in the chest of Pettenkofer's respiration-apparatus. This was arranged so that by setting it in action from time to time for 24 hours, the products of respiration during the 12 hours of day, could be separated from those of the 12 hours of night. The increase or decrease of the animals in weight was noted daily.

The excretion of CO_2 by the animals was different during the daytime from that during the night; the difference was determined, however, not by the time of day as such (light and darkness), but by the distribution of food during the two halves of the day. With a preponderance of food during the daytime, more CO_2 was excreted in the day than during the night, and *vice versâ*, so that an increased consumption of 1 gram of hay was followed by an increased excretion, on

* Chem. Centr., 1871, 348.

the average, of 0·11 to 0·12 gram of CO_2. It follows, that to obtain normal numbers for the respiration-products of 24 hours, with the slowly digesting ruminants, it is necessary to extend the experiments on respiration over both the day and night; and that it is unadvisable to continue an experiment for a shorter period than 24 hours.

The excretion of water by the skin followed, on the whole, the same rule as that of the carbonic acid excretion. It was different in the two halves of the 24 hours, and was greatest in that portion of the day when the animal took the largest quantity of food. There was usually a parallelism observed between the excretion of CO_2 and of water in 24 hours, both these excretions, under similar circumstances, being greater or less, accordingly as the consumption of respiration material, or, in other words, of nutriment, was greater or less. It is therefore necessary to protect the animal from conditions which induce perspiration, if it be desired to economise food.

Increased external temperature determines, on the one hand, increased consumption of water, and, in consequence, increased transudation of water through the skin of the animal, and, on the other hand, diminution of the loss of heat of the body through conduction and radiation. In consequence of these antagonistic relations, the minimum consumption of nutritive material, and, consequently, the greatest tendency to increase of the animal will, other circumstances being equal, be associated with a certain medium temperature of the stall in which the animal is fed.

The inspiration of atmospheric oxygen and its expiration in the form of respiration-products, especially CO_2, did not proceed *pari passu.* Most commonly the one process increased or diminished beyond the other for a time, and an equilibrium was obtained only after a considerable period.

Complete deprivation of food (drink being taken) for a single day reduced the production of CO_2 and excretion of water by the animal to nearly one-half, and in such a manner that the decrement in that half of the day nearest the preceding one on which food had been taken, was much less than in the more distant half of the day.

These researches showed that the food consumed was slightly greater than that required to keep the body in *statu quo*, along with a normal growth of wool, but not to an extent which had any real significance. The atmosphere contributed only one-sixth part to the material received; but, on the other hand, laid claim to nearly one-half of the material excreted. More than one-half of the organic substance of the food fell, directly or indirectly, to the process of respiration, whilst the growth of new wool absorbed not one per cent. of it. About eight-ninths of the residue were found in the fæces, and one-ninth in the urine.

Of the atmospheric oxygen taking part in the waste of tissue, 3·5 per cent. went towards the formation of water, and 96·5 per cent. towards the formation of CO_2, and, consequently, the oxygen excreted in the form of CO_2 was nearly equal to that removed from the atmosphere. This is a necessary consequence of the circumstance that the organic substances destroyed by the process of respiration, are, as their empirical formula, $C_{24}H_{41}O_{19}$, shows, very near the carbo-hydrates in their elementary composition. The near accordance of the oxygen received with the oxygen excreted in the form of CO_2, is characteristic of herbivorous animals.

The generation of heat by the animals, due to oxidation-processes, was equivalent to 42,000 heat-units (each = 1 gram raised from 0° to 1°) per day per kilogramme of weight of body.

The distribution of the various mineral constituents of the food on their reappearance in the fæces and urine, corresponded on the whole, though not exactly, with their respective solubilities and dialytic relations. The two alkaline-earths, lime and magnesia, appeared in relatively large proportions in the fæces—the lime in greater proportion than the magnesia. Similarly with the two alkalies and the urine, the potash was recovered therefrom in greater proportion than the soda. Of the phosphoric acid, scarcely more than a trace was found in the urine. T. S.

On Artificial Digestion of Casein by Pepsin, and the Action of Water on Albuminous Substances. By N. Lubavin.*

After giving a short sketch of the history of digestion, Lubavin details five experiments on the digestion of casein and albumin by artificial gastric juice, prepared by treating the mucous membrane of a pig's stomach with water containing ·3 per cent. of hydrochloric acid. The casein was obtained by precipitating it from milk by acetic or hydrochloric acid, and freed as much as possible from fat by means of ether. A small amount of fat always remained attached to it, and could never be entirely removed. The casein was digested for periods varying from 5 hours to 11 days. During a great part of this time, the fluid was kept at a temperature of 40° to 45°.

A great part of the casein was thus dissolved, but however long the digestion was continued, a portion still remained undissolved. The amount of this was smaller when the casein was prepared with hydrochloric instead of acetic acid. When serum albumin and casein were digested for equal times, one-third less albumin than casein was dissolved.

In the digested solution the author found pepsin, peptones, leucine and

* Med. Chem. Untersuchungen, 1871, 463—484.

tyrosine. By treating an alcoholic extract of the products of digestion with baryta-water, he obtained a brown transparent deliquescent mass, which he thinks is a compound of peptone with barium.

When purified by alcohol and ether, it forms a white non-deliquescent powder, containing chlorine. The proportion between the chlorine and barium is by no means constant.

If this were a definite compound of barium and peptone, the equivalent of peptone would be 424, indicating a tolerably simple composition.

The specific rotatory power of this substance is $-63{\cdot}2°$, or if the chlorine and barium be regarded as inactive, and the rotation calculated for the organic substance alone, it would be $-84°$. By precipitating the barium compound with zinc sulphate or cupric sulphate, compounds of peptone with zinc or copper were obtained. The undigested residue of the casein, the dyspeptone of Meissner, consists of two substances, one of which A is soluble, and the other B is insoluble in sodium carbonate. When A is precipitated from this solution by hydrochloric acid, it is found to be in a great measure dissolved if digested anew with gastric juice, but a certain amount of residue always remains. After this is purified by alcohol and ether, it forms a yellowish white dusty powder containing C. 48·5, H. 7·1, N. 13·3, P. 4·6 and O. 20·5 per cent., which would nearly correspond with the formula $C_{27}H_{47}N_6PO_{11}$.

When moistened with water, it has an acid reaction, and seems partly to expel CO_2 from sodium carbonate. On dry distillation it gives off an irritating smell, not at all like that of albuminous substances. These properties, along with its composition and simple formula, show that it is not albuminous. The substance B resembles albumin in its reactions, and contains sulphur and phosphorus, but he has not yet determined its exact composition.

As to the nature of these bodies, he considers that although the substance B might possibly be an isomeric transformation of casein, the substance A cannot be so; and that they are products of the decomposition of casein, and not mere mechanical admixtures, he considers to be shown by the fact that casein, when combined with hydrochloric acid before digestion, was soluble in water, but after digestion yielded a substance insoluble both in acids and water,—and by the observation of Völckel that casein precipitated from milk by saturated solution of common salt contains an amount of phosphorus larger than that which corresponds to the phosphate of lime in the ash.

Casein thus consists, like vitellin and hæmoglobin, of an albuminous in combination with a non-albuminous body. As a body containing phosphorus exists in it, and albuminates can be prepared from white of egg which contains no phosphorus, it is not identical as is commonly supposed with albuminates prepared from other albuminous bodies.

By heating serum albumin with water in a Papin's digester to 120° —150° C. for 26 hours, he obtained leucine with a trace of tyrosine, and on heating casein with water to 200° for 10 hours in sealed tubes, he got leucine with a considerable amount of tyrosine.

Casein heated with glacial acetic acid to 180° in sealed tubes, yielded tyrosine and sulphuretted hydrogen.

From his experiments and those already made by others, he believes that the decomposition of albuminous bodies, whether by putrefaction or by the action of water, acids, or ferments, consists in their taking up water and splitting up first into peptones and then into leucine and tyrosine.

T. L. B.

On Pepsin. By E. HEINTZ (Arch. Pharm., cxlvi, 130).

On the Action of Hydrochloric Acid on Ossein. New Researches on the Determination of Ossein in Fossil Bones. By A. SCHEURER-KESTNER.*

I. FOSSIL bones often contain so small a proportion of gelatigenous matter, that considerable quantities of bone must be employed for solution of the mineral matters in hydrochloric acid. The author has sought to determine the influence of this acid, dilute as well as concentrated, on ossein, in order to determine whether the soluble ossein, the existence of which he has previously announced, exists ready formed in the bones, or is formed by the prolonged action of dilute hydrochloric acid on ordinary ossein. The existence of a certain quantity of soluble ossein in fossil bones appears to him to be placed beyond doubt, not only by his analyses, but also by the fact that he has extracted it directly from the bones by triturating them with pure water. Nevertheless, the criticisms of Élie de Beaumont have induced Scheurer-Kestner to seek to determine in a more rigorous manner the proportions of the two osseins.

II. Ordinary ossein, in a state of purity, prepared by Frémy's method, dissolves completely in the course of a few hours in cold concentrated hydrochloric acid. This solution, when freed from hydrochloric acid by silver nitrate, is neutral, and exhibits neither the properties of gelatin nor of those of any of its known derivatives. When it is evaporated, and the residue calcined, an odour of burnt horn is developed. It is not precipitated by any of the salts which precipitate gelatin; and on concentration neither a jelly is produced, nor crystals.

Weak hydrochloric acid exerts no influence on ossein; but for this

* J. Pharm. [4], xiii, 111.

purpose the solution employed must not contain more than one-half per cent. of real acid. Hence the acid recommended by Frémy for the estimation of ossein (1 vol. ordinary acid to 9 vol. water) has a sensible solvent action on ossein.

III. For the purpose of estimating the two osseins, an acid containing not more than one-half per cent. of real acid was employed. The bone of a mammoth yielded—

	Grams.	Composition of the animal matter.
Ordinary ossein	0·617	63·7
Soluble ossein	0·352	36·3
		100·0

The bone of an *Ursus spelæus* gave:

Ordinary ossein	0·204	37·4
Soluble ossein	0·342	62·6
		100·0

This soluble ossein is not formed—at least not altogether formed—by the action of hydrochloric acid on ordinary ossein.

IV. The paper concludes with some remarks on the criticisms of Elie de Beaumont on a previous paper by the author establishing the identity of the ossein of recent with the ossein of fossil bones.

T. S.

On the Behaviour of Animal Substances containing Phosphorus when undergoing Decomposition. By P. Plósz.*

The solution of the question, whether vegetable and animal substances containing phosphorus give off phosphoretted hydrogen when undergoing putrefaction, is a subject of great practical, as well as high scientific interest. If it were answered affirmatively, it would show either that phosphorus exists in the organism in some other form than that of phosphoric acid, or that, under the influence of putrefaction, reducing substances are formed of so energetic a nature, that even phosphoric acid is deprived of its oxygen. It is difficult to conceive that either of these things should happen. In the animal organism energetic processes of oxidation go on: hence lower degrees of oxidation cannot arise, nor combinations of phosphorus with other elements, for such combinations would be quickly oxidised into phosphoric acid.

The vegetable organism has the property of reducing certain compounds; but whether it is able to deprive phosphoric acid (and plants

* Med. Chem. Unters., 1871, 521.

find phosphorus exclusively in this form) of its oxygen, is as doubtful as the reduction of phosphoric acid during putrefaction.

The experiments of the author were carried out under Hoppe-Seyler's supervision, preliminary to more extended researches, and led to the following results:—

Fishes were taken for the purposes of experiment, as it appeared that these animals were best adapted for the purpose, not only on account of the large proportion of lecithine which they contain, but also because it is probable that they contain another phosphorised body in the nuclei of their blood corpuscles. The fishes were beaten to a pulp and set aside with a little water for putrefaction to set in. The external air was excluded, so that only that air which was contained in the flask could act as an oxygenant. A disengagement of gas quickly took place. The gas given off was conducted through a solution of silver nitrate, in which it produced a dark brown precipitate. The generation of gas ceased after some time, but was renewed as soon as air was admitted into the apparatus. In this manner four parallel experiments were made, and the whole precipitate formed during a period of five weeks was employed in the examination for phosphorus and sulphur. For this purpose the precipitate was acted upon with nitro-hydrochloric acid, every precaution being taken, and tested for sulphuric and phosphoric acids. Sulphuric acid was found in abundance, but no phosphoric acid could be detected.

T. S.

On the Condition of the Doubly Refractive Substance of Striped Muscular Fibre. By P. Plósz.*

An interesting paper on the microscopic appearances of muscular fibre, including full descriptions of the observations of the author, as well as those of previous observers, on the isotropic and anisotropic substances, disdiaclasts, &c. The following is of chemical interest:—

The disdiaclasts exhibit a peculiar reaction. Solutions of neutral salts, as sodium chloride, sodium phosphate, and sulphate, &c., which dissolve myosin, do not affect the doubly refractive power of muscular fibre in the least; and if the fibre be unravelled as much as possible with the forceps and drawn through a solution of common salt, it is completely deprived of myosin without losing its doubly refractive power. Nevertheless, muscle cannot be thus freed from all albuminous bodies. If now the muscular fibre, deprived of myosin be treated with a solution of hydrochloric acid containing 0·1 per cent. of the acid, or with a dilute solution of sodium carbonate, an albuminous body goes

* Med. Chem. Unters., 1871, 510.

into solution, which at first gives all the reactions for myosin, but after some standing in acid solution changes into syntonin, in alkaline solution into alkaline albuminate.

This peculiar behaviour of a portion of the albuminous substance of muscle can with difficulty be explained in any other manner than upon the assumption that a part of the myosin in muscular fibre is in chemical combination with another unknown substance, and that this compound is decomposible by acids or alkalies, but not by neutral salts.

On this hypothesis the actions of acetic, sulphuric, and hydrochloric acids, as well as of carbonated and caustic alkalis, are similar, only the myosin is most readily changed by hydrochloric acid into syntonin, by caustic potash or soda into alkaline albuminate—facts already well known. T. S.

Contributions to the Knowledge of the Blood of Man and Mammals. On Hæmatin. By F. HOPPE-SEYLER.*

HÆMATIN is best obtained from crystals of hæmin, which the author obtains by a method essentially the same as that given by Teichmann. Hæmatin differs little in appearance from hæmin. Its formula is given as

$$C_{68}H_{70}N_8Fe_2O_{10}.$$

Hæmin, which is the hydrochloride of hæmatin, appears to have the formula—

$$C_{68}H_{72}N_8Fe_2O_{10}Cl_2.$$

This formula for hæmatin differs from that given by Mulder. Mulder's formula is $C_{44}H_{44}N_6FeO_6$, requiring only 6·93 per cent. iron, a result which Hoppe-Seyler shows to be due to the fact that hæmatin obtained by the method employed by Mulder, is an impure substance.

Among the properties of hæmatin is its power in aqueous or alkaline alcoholic solutions to absorb the violet rays, but especially the yellow rays between the lines C and D of the solar spectrum—nearer the latter. The solutions of hæmatin in alcohol containing sulphuric acid give more or less sharply defined absorption bands in different parts of the spectrum. One characteristic band occurs between C and D—nearer C.

Action of Concentrated Sulphuric Acid on Hæmatin.—The author's experiments lead to a different view from that held by Mulder and van Goudoever. According to them, the sulphuric acid first combines

* Med. Chem. Untersuch., 1871, pp. 523—550.

with the hæmatin, and on the addition of water the iron enters into combination with the sulphuric acid, while the hydrogen displaced by the iron is evolved, leaving non-ferruginous hæmatin, whose formula they give as $C_{44}H_{44}N_6O_6$. Hoppe finds no trace of hydrogen evolved by the action of sulphuric acid on hæmatin. When the solution of hæmatin in sulphuric acid is filtered through asbestos, a beautiful purple-red solution is obtained, which gives a small, dark, absorption-band just before the line D, and another very sharply defined band between D and E. When this solution is mixed with water, the greater part is precipitated, the precipitate being increased by the addition of alkalies to neutralisation. The alkaline watery solutions of the precipitate are characterised by a faint band between C and D, a similar faint band between D and E—nearer D, a darker in the same situation but nearer E, and lastly, a very dark band between *b* and F.

The formula of the substance is calculated as $C_{68}H_{74}N_8O_{12}$. Its formation from hæmatin is represented by the equation—

$$C_{68}H_{70}N_8O_{10}Fe_2 + 4(SO_4H_2) + O_2 = C_{68}H_{70}N_8O_{10}(SH_2O_4)_2 + 2(FeSO_4) + 2H_2O.$$

The compound $C_{68}H_{70}N_8O_{10}(SH_2O_4)_2$ being subsequently converted by the action of water in excess into $C_{68}H_{74}N_4O_{12}$. The formation of this substance requires the presence of oxygen.

If, on the other hand, hæmatin is acted on by sulphuric acid in closed vessels, a substance is formed, only very slightly soluble in sulphuric acid, and quite insoluble in caustic potash. Its formula is calculated as $C_{68}H_{78}N_8O_7$.

In the absence of a more complete knowledge of these products, the author calls the first, which is soluble both in sulphuric acid and caustic potash, *hæmatoporphyrin* ($C_{68}H_{74}N_8O_{12}$), and the second, insoluble in caustic potash, *hæmatolin*.

Action of Reducing Agents on Hæmatin.—Hæmatin offers considerable resistance to oxidising agents. It is, however, very sensitive to reducing agents, both in acid and alkaline solutions. By boiling a solution of hæmatin with caustic soda and zinc filings, as also by the action of sodium amalgam on hæmatin in presence of water, reduction products in great quantity are formed. They are all free from iron, but their separation is a matter of great difficulty. Their solution gives a complicated spectrum, with five absorption bands. No exact analysis can be given.

Action of Tin and Hydrochloric Acid.—These substances act on hæmatin, in presence of alcohol, differently, according as the hæmatin is fully dissolved or not. When a concentrated solution, or one containing excess of hæmatin, is heated with tin or copper or zinc

on the water-bath, a purple-red solution, with, after a time, a resinous dark violet precipitate is formed. The solution is characterised by two dark absorption-bands between D and E. When hæmatin, or hæmin crystals dissolved in alcohol containing sulphuric acid, are decomposed by hydrochloric acid and tin, and heated, a purple solution is formed, which also has a characteristic spectrum, viz., one band between D and E, another just before D, and another broad band between *b* and F, covering the latter line. When the evaporated solution is poured into boiling water, a brownish precipitate is formed, soluble in alcohol. This on evaporation yields a colouring matter, which in properties resembles the oxidized product obtained by distillation from the hæmatin reduced by zinc filings.

The formula of the substance appears to be $C_{34}H_{49}N_3O_7Cl$, a substance which the author thinks will, on more exact investigation, throw great light on the chemical constitution of hæmatin.

Behaviour of Hæmatin when treated with Phosphorous Chloride containing free Phosphorus.—When hæmin crystals are heated with this substance to a temperature of 140°, in closed tubes for 6—8 hours, a purple-brown fluid is formed, which gives a spectrum with three absorption-bands, one between C and D, close to C, a second between D and E—nearer E, and a third between *b* and F, beginning from *b*, and extending to the middle between *b* and F. No evolution of gas follows the opening of the tube. A crust forms on the sides, which, however, is easily separated. This substance is to a certain extent soluble in water, giving the same spectrum as hæmatoporphyrin. From the part insoluble in water a substance is obtained resembling hæmatin. The formula of this substance appears to be $C_{68}H_{70}N_8O_{10}(PO_4H_2)_4$. The agreement of this substance with hæmatoporphyrin in its spectrum points to the formula of the latter as $C_{68}H_{70}N_8O_{10}.2(H_2O)$, *i.e.*, a hydrate of the same complex of atoms as is contained in the phosphate.

Decomposition of Hæmoglobin in absence of Oxygen.—As the author has already described, hæmatin is no distinct product of the splitting up of hæmoglobin, but results from such a decomposition, accompanied by oxidation. The oxidation takes place so rapidly, however, that precautions must be taken in order to obtain the non-oxidized products.

The author describes a very ingenious arrangement by which a solution of hæmoglobin can be reduced by hydrogen and decomposed by alcohol containing sulphuric acid or caustic potash, in absence of oxygen. A colouring matter is produced, which has a purple-red colour, both in acid and in alkaline solutions, and is characterised by certain definite absorption-bands. It is this substance, called by the author *Hæmochromogen*, which on oxidation forms hæmatin.

Hæmoglobin, therefore, seems to be a compound of an albuminoïd substance and a group of atoms, which, on splitting up, yields hæmochromogen. The two are apparently loosely combined together. Hæmochromogen as such cannot exist free in the blood-corpuscles, for then hæmatin would result on access of oxygen.

The mode in which the albuminoïd, and the group which yields hæmochromogen, are combined, is such as to resist the fixation of oxygen, and it may be supposed that it is just at the point of resolution of the combination that the rapid absorption of oxygen takes place.

The author has not succeeded in isolating hæmochromogen for analysis, or of regenerating it by reducing hæmatin. The spectrum of reduced hæmatin (Stokes) agrees with that of hæmochromogen, but it is impossible to say whether the two substances are identical.

The formation of hæmatin from hæmochromogen may be supposed to take place as follows:—

$$2C_{34}H_{36}N_4FeO_5 + O = C_{68}H_{70}N_8Fe_2O_{10} + H_2O;$$

and from the compound of hæmochromogen with carbonic oxide, as follows:—

$$2(C_{34}H_{36}N_4FeO_5.CO) + O_3 = C_{68}H_{70}N_8Fe_2O_{10} + 2CO_2 + H_2O.$$

Hæmatin seems to be formed when concentrated solutions of hæmoglobin are allowed to stand, but instead of being precipitated, it enters into combination with albuminoïds. Such apparently is the nature of metahæmoglobin. It is still doubtful whether the iron exists in the colouring matter of blood as a ferrous or as a ferric salt. It is probable that in hæmatin it is the latter condition. The proportion of oxygen to iron in oxyhæmoglobin is such that for each atom of iron there are two atoms, or one molecule, of oxygen.

In Lothar Meyer's researches it was found that when blood was decomposed by an acid before heating, and before the evacuation of oxygen, only $\frac{1}{5}$—$\frac{1}{2}$ of the quantity was obtained, as compared with the amount obtained by the usual method. It would therefore appear that, by the conversion of hæmochromogen into hæmatin, only $\frac{1}{2}$ or $\frac{1}{4}$ of the oxygen which hæmoglobin can fix loosely, enters into stable combination. This quantity would harmonise with the supposition that in this decomposition the iron passes from the state of ferrous to that of ferric oxide.

In closest relation to hæmoglobin is a brownish colouring matter, identical with or closely allied to metahæmoglobin, found in cystic fluids, &c.

The black pigment of the lungs and bronchial glands, and also the

stellate pigment-cells of amphibia, seem to be a residue of hæmatin, while biliary and urinary pigments appear to be products of hæmochromogen or venous hæmoglobin. In atomic relations there is a very close affinity between hæmochromogen and bilirubin. There are numerous facts which favour the view that bilirubin is formed by the action of water and an acid on hæmoglobin in absence of oxygen.

D. F.

On the Chemical Relations of the Nuclei of Blood-corpuscles in Birds and Snakes. By P. Plösz.*

In this research Dr. Plösz has somewhat improved the method and confirmed the results already published by the abstractor of this paper. In addition to freeing the nuclei from the substance of the blood-corpuscles by means of water and ether, he removes the last traces of it by washing with dilute hydrochloric acid and warm alcohol and ether, sometimes with and sometimes without previous digestion in artificial gastric juice. The nuclei in the blood of birds and snakes consist of the same substance, but he could not discover it in ox-blood. This substance is indigestible, and gives the reactions of mucin, but differs from it in being insoluble in dilute mineral acids, and in containing 2·4 per cent. of phosphorus.

T. L. B.

On the Composition of the Blood in Chyluria. By F. Hoppe-Seyler.†

The author has been fortunate enough to obtain at the same time specimens of the blood and urine of a lady (a patient of the late Prof. Niemeyer) labouring under chyluria. The urine had a milky-white appearance, and contained over 0·7 per cent. fat. The blood, which was obtained by cupping, coagulated completely, so that 83·325 grm. blood gave 35·245 grm. pure serum. The serum was yellowish, scarcely turbid, and not at all milky, and therefore not of the same fatty nature as the urine. Without quoting the tables of the analysis of the serum at length, the general result seemed to be that there was a smaller proportion of albuminoïds than usual. This might be due to the loss by the urine, or to the admixture with lymph, owing to the way in which the blood was obtained, or to both, as Hoppe suggests.

In respect to cholesterin, lecithine, and fat, the quantity, 0·75 grm. in 100 seems high. Of this, 0·36 grm. being pure fat indicates a high percentage of fat in the serum. As regards the salts, sodium chloride

* Med. Chem. Untersuch., 1871, 461.
† Med. Chem. Untersuch., 1871, pp. 551—556.

appeared somewhat small in amount. The amount of phosphate of soda was especially low, a fact to be explained by the method of analysis after extraction of the lecithine. The blood-clot weighed 48·080 grm. The amount of hæmoglobin was determined by comparison with a solution of guinea-pig hæmoglobin of known percentage.

The amount of cholesterin and lecithine was much greater in the clot than in the serum. A small amount of fat was found, due, as shown by the author, to the presence of serum still entangled in the clot; hence the blood-corpuscles in chyluria do not appear to contain fat any more than normal corpuscles.

The extractions of the clot scarcely differed from those of the serum. Sulphate of soda was much larger in amount, and the amount of phosphate of soda was three times as much as in the serum. The amount of alkaline carbonates was likewise greater.

The whole blood gave the following composition—

		In 83·325 grm. blood.	In 100 grm. blood.
Hæmoglobin		12·4600	14·960
Albuminoïds	Fibrin	0·2327	0·279
	Soluble albuminoïds	2·5633	3·075
Ethereal extract	Cholesterin	0·1315	0·158
	Lecithin	0·2903	0·348
	Fats	0·1414	0·170
Extractives	Soluble in alcohol	0·1833	0·220
	Insoluble	0·3447	0·414
Salts	Chloride of potassium	0·1713	0·206
	Chloride of sodium	0·2085	0·250
	Sulphate of soda	0·0622	0·075
	Phosphate of soda	0·0360	0·043
	Carbonate of soda	0·0245	0·029
	Phosphate of lime / Phosphate of magnesia	0·0793	0·095
Total solids			20·322

As to whether the amount of hæmoglobin was normal or not, it is difficult to say, owing to the want of exact determination of the amount of hæmoglobin in normal blood.

The method by incineration and estimation of the iron gave results which were too low, and the colour method is apt to give too high results.

Apart from this, however, it is evident, from the percentage of hæmoglobin found, that in chyluria the amount of blood colouring matter and blood-corpuscles is not diminished. As the whole blood

contained 0·17 per cent. fat, the serum 0·359 per cent., while the urine contained 0·72 per cent., it is evident that the fat in the urine is not derived from transudation alone, but that a corresponding amount of transudate free from or poorer in fat finds its way back either into the lymph or into the blood-vessels.

D. F.

The Chemical Composition of Pus-corpuscles. By F. MIESCHER.*

IN order to obtain pus-corpuscles free from serum, the pus and articles soaked with it, such as surgical bandages, were treated with a mixture of 1 part saturated solution of sodium sulphate with 9 parts water, except when the alkalies of the ash had to be determined, in which case a saturated solution of barium nitrate diluted one-half was employed.

In these fluids the pus-corpuscles sink to the bottom, and after repeated washing are obtained sufficiently pure, while the supernatant liquid is tolerably free from turbidity.

The Albuminoïds of the Protoplasm.—Pus-corpuscles are composed chiefly of albuminoïds. When treated with a solution of sodium chloride of 3—10 per cent., they are converted into a gelatinous viscous mass. This depends, as Rovida has shown, on the formation of a ring of hyaline substance round each cell. This mass, diluted with water, gives a ragged precipitate, and was supposed by Hoppe to indicate myosin. Miescher, however, can obtain no trace of myosin reaction. None of the hyaline substance appears soluble in water, and therein he differs from Rovida. In other respects his results agree with those of Rovida.

The constituent albuminoïds appear to be—

1. Alkali-albuminate, partially precipitated by carbonic acid, more completely by acetic acid, insoluble in common salt, soluble in hydrochloric acid ($\frac{1}{1000}$). Whether it is kept in solution by alkaline phosphate could not be determined on account of the extreme dilution.

2. An albuminoïd coagulable at 48—49°. The flocculi are insoluble in hydrochloric acid ($\frac{1}{1000}$), in sodium chloride, and also in very dilute soda solution. It is therefore not merely albumin dissolved in a phosphate.

3. An albuminoïd coagulable at the ordinary temperature of serum albumin.

In addition to these—

4. Rovida's hyaline substance, an albuminoïd insoluble in water, soluble in hydrochloric acid ($\frac{1}{1000}$), swelling up in solution of sodium chloride.

* Med. Chem. Untersuch., 1871, 441—460.

5. An albuminoïd unaltered in water, and sodium chloride, with difficulty soluble in hydrochloric acid ($\frac{1}{1000}$).

The substances thus agree, as far as number is concerned, with the five different albuminoïds found by Kühne in muscle. The author has not been able to find paraglobulin, though he admits the possibility of its presence.

The Alcoholic Extract.—When proper precautions are taken, a nearly colourless solution is obtained by heating the corpuscles with strong alcohol at a temperature of 50°—60°. Miescher has only investigated the extract with reference to the presence of lecithine and cerebrin.

The greater part of the alcoholic extract is also soluble in ether. From the amount of phosphoric anhydride in the extract (3·804 per cent.) the amount of lecithin is calculated according to Diakonow's formula. The author estimates it as 44·28 per cent. of the whole extract, or 17·8 per cent. of the dry pus corpuscles. This is not very far different from the amount found by Parkes in the yolk of egg (protagon 52 per cent. = 20·7 per cent. lecithine).

By treating the portion insoluble in ether with sulphuric acid, he obtained a substance which gave the sugar reaction. This indicates the presence of cerebrin or a similar substance.

The Watery Extract.—The corpuscles after extraction with alcohol were repeatedly tested for glutin and chondrin without success.

The Ash.—The ash was analysed according to Hoppe-Seyler's method.

In 100 parts of dry pus-corpuscles there were found—

NaCl ..	0·1428;	Na_2O ..	0·2625
K_2O ..	0·6546;	CaO ..	0·830
MgO ..	0·0870;	Fe_2O_3 ..	0·0390 = 1·2689.

The amount of phosphoric acid was found to be in one case 2·689 per cent., and in another 2·778 per cent. of the dry substance. Chlorine is also present. In relation to the question of the conversion of colourless into coloured corpuscles, the amount of iron seems small, but it is probable that, relatively to the larger size of the white corpuscles, the amount of iron may be sufficient to account for the greater part found in the blood colouring matter.

The Nuclei and Nuclein.—After several attempts to isolate the nuclei, Miescher found that he could succeed by shaking the corpuscles, which had undergone prolonged treatment in the cold in dilute hydrochloric acid, in a mixture of ether and water. Ultimately a fine powder settled to the bottom of the watery stratum, which powder consisted of pure nuclei preserving their microscopic characters.

The nuclei agree for the most part in their reactions with mucin.

Another method of isolating nuclei is to digest the pus-corpuscles, after previous digestion in warm alcohol, in a pepsin solution, made from an extract of pig's stomach containing 1 per cent. strong hydrochloric acid. The nuclei remain while the rest of the corpuscle is digested away.

The nuclei, except that they are more shrivelled and granular, resemble those obtained by the former method.

The nuclei consist of a substance soluble in dilute soda solution, and another insoluble—soluble and insoluble nuclein. The nuclei are entirely soluble in strong hydrochloric acid and caustic alkalies.

The substance of the nuclei contains nitrogen and sulphur, and is very rich in phosphorus, which is a real organic constituent. Miescher considers that in nuclein we have no mixture of substances, such as at first sight might appear, but really a substance *sui generis*. He further makes some interesting observations on the part phosphorus plays in cell growth, and the probable genesis of the cell albuminoïds and their derivatives, for which we must refer to the original paper.

D. F.

The Chemical Composition of Pus. By F. Hoppe-Seyler.*

Hoppe-Seyler agrees with the results obtained by Miescher, which he regards as the most important contribution made of late years to the chemistry of pus.

On the Phosphoretted Substances in Pus.—Phosphoretted substances were first clearly demonstrated by Fischer in pus, and identified with Liebreich's protagon.

Miescher regards this substance as a mixture of lecithine and cerebrin, and in this respect Hoppe agrees with him, regarding the relation between them as precisely similar to that which obtains in nerve tissue.

Miescher has also demonstrated the presence of another substance containing phosphorus in the nuclei of pus-corpuscles. His method of isolating the substance has already been given.

In relation to the researches of Lubavin, Hoppe inquired whether Miescher's nuclein might not be a peptone produced by action of the artificial gastric juice.

From his investigations he arrives at the conclusion that nuclein, as such, exists preformed in the pus-corpuscles, and is not the mere product of digestion. In its relation to pepsin solutions, nuclein appears to be allied to amyloïd substance; and he thinks it is not impossible that in certain conditions amyloïd substance may be formed from nuclein.

* Med. Chem. Untersuch., 1871, 486—501.

Nuclein closely resembles mucin. It appears, however, to be richer in phosphorus. As regards the quantitative composition of pus, Hoppe has made numerous analyses, and tabulates the results.

The constituents of pus-serum agree with those of blood-serum and transudate fluids generally. Pus-serum is always cloudy: the dispersion of light depends slightly on fluorescence, as shown by examination with a Nichol's prism.

He finds no glutin or chondrin in pus-serum or pus-corpuscles, and likewise no chloro-rodic acid—all which substances are stated by Bödeker to exist in pus.

On the Origin and Ultimate Fate of Pus-corpuscles and Serum.—In reference to the question of the origin of pus-corpuscles and their identity with the colourless and lymph-corpuscles, Hoppe's results are very interesting.

As it is impossible to obtain living colourless corpuscles from the blood in sufficient quantity for chemical analysis, the spleen was taken and analysed for glycogen in the usual way. Both glycogen and cerebrin were found. Probably the cerebrin might be due to the presence of dark-bordered nerve-fibres in the spleen, and the glycogen to the non-voluntary muscular fibres. More satisfactory results therefore were obtained by the method of introducing fresh crystalline lenses of the ox, which contain no cerebrin or glycogen, into the abdominal cavity of dogs, and analysing them after a period varying from 1—24 days.

As was expected, the lenses became infiltrated with lymph corpuscles.

The presence of glycogen was proved most distinctly in the lenses removed after the eighth day, which period corresponded with the greatest number of active cells. Less clearly was it found after three days, and not at all on the first or fourteenth day.

The conclusion is, that the glycogen comes from the lymph-corpuscles. If the lenses are not immediately plunged into boiling water, but allowed to stand until the lymph-corpuscles become rigid, then no glycogen is found, but in its place sugar.

In the pus of congestion-abscesses and wounds, no glycogen was found. The occurrence of glycogen therefore may be taken as a means of distinguishing lymph from pus-corpuscles, although the latter spring from the former.

If glycogen is found in suppurating wounds, it will aways coexist with the presence of numerous contractile corpuscles. In reference to the nature of the fatty degeneration of pus, and the occurrence of histolytic products, such as leucine and tyrosine, the results may be stated briefly. Lymph-corpuscles, by their transformation into rigid pus-corpuscles, lose their glycogenic properties, and by excess of oxygen

may produce fat. In addition to this, stagnant pus may, by maceration in water, undergo many changes in composition, which changes proceed more rapidly on access of oxygen, and result in several oxidation products. Yeast-cells and pus-corpuscles in many respects seem very closely allied, and there appears to exist in yeast a substance identical with the nuclein of pus.

The occurrence of secondary and oxidation products is similar in both. D. F.

On the Nuclear Structures in the Yolk of the Hen's Egg. By Dr. F. MIESCHER.*

THE nature and physiological signification of certain structures in the egg, have been the subject of much discussion among histologists and embryologists for several years. In the present paper Dr. Miescher gives the results he has arrived at by the method of investigation which he has applied so successfully to the chemistry of pus.

In the yolk two elements are met with; the yellow which constitute the chief part of the yolk, and the white yolk-elements. These latter are found chiefly under the yolk membrane, round the germinal vesicle, and in a process extending from this into the centre of the yolk.

The white yolk-elements differ much in size and appearance. They possess distinct cell-membranes and homogeneous contents. Within this is found a peculiar spheroidal, solid, strongly refractive body. Sometimes more than one, and sometimes a great number exist varying in size down to molecular fineness.

Whether these bodies are cell-nuclei has been much discussed.

Their insolubility in ether and alcohol shuts out the idea of their being merely fat globules. Their histochemical reactions indicate an albuminoïd in some such allied substance. They differ from the cell contents by being insoluble in salt solutions.

To decide their nature, Miescher adopted the following method of procedure:—

The yolk was freed from membrane as far as possible, extracted with ether and then treated with boiling alcohol four times in four successive hours. The residue was boiled with water to get rid of the alcohol, and then subjected to digestion with pepsin. As an indigestible residue, a ponderny white deposit remained, while the supernatant fluid remained clear. This deposit was washed till all turbidity with tannin ceased, then extracted with warm alcohol and ether in order to get rid of any traces of lecithin or histolytic products which might have been produced by the process of digestion.

* Med. Chem. Untersuch., 1871, 502—509.

The deposit so treated was found to consist chiefly of flakes or conglomerations of granules of various shapes and sizes, which could be none other than the peculiar nuclear-like bodies of the yolk-elements. Some of these had the same appearance as in the fresh yolk, others were variously changed; which change Miescher attributes to the extraction of certain of their constituents.

The so-called nucleoli of his, and the yellow colouring matter of Dursy, are among the substances so extracted by alcohol. These nuclei are soluble in a one per cent. solution of sodium carbonate forming a more or less opalescent fluid which, with the exception of a few fat globules, contains no structural element. The solution is precipitated by acetic acid and dilute hydrochloric acid just like the solution of pus nuclei.

The precipitate gives the xanthoprotein reaction a violet colour with potash and sulphate of copper, and a faint red with Millon's reagent. In other respects also it agrees with pus nuclein. Alcohol dissolves a small portion, and also ether. A rare property for a substance allied to albumin.

The dry substance yields phosphorus in large quantity.

In one case 0·3583 grm. nuclei gave 15·35 per cent. phosphoric acid.
In another 0·2985 grm. „ 16·23 „ „

In the first case the nuclei were obtained from a soda solution by precipitation with acetic acid; in the second by digestion.

When the substance is carefully heated till all ammoniacal vapours have disappeared, a bulky coke is left which, with the exception of 5·03 per cent. phosphoric acid, and a trace of silica gives no ash.

The quantity of phosphorus obtained in this way is only one-third the whole quantity contained in the substance. The rest had disappeared. This indicates a peculiar organic combination of the phosphorus; a phosphoretted albuminoïd substance, like the nuclein of pus. There seems, therefore, no doubt as to the nuclear nature of these bodies in the yolk elements.

The quantitative relation of the nucleus to the rest of the cell is interesting. From one yolk Miescher always obtained from 0·2—0·5 grm. dry nuclein. A yolk weighs about 15—20 grm. Hence of 15 per cent. albuminoïd substance contained in the yolk, 1—1·5 per cent. at least is nuclein—a relation of nuclein to protoplasm which is higher than in the pus corpuscle. As the white yolk elements are small in quantity as compared with the yellow, it must follow that the yellow are not non-nucleated structures. Probably their nuclei exist as fine molecules; a condition of nuclei of great histological signification.

D. F.

Physiological Action of Chloral Hydrate. By H. BYASSON.*

CONCLUSIONS are derived from these experiments on the physiological action of chloral hydrate on frogs, rats, and cats, contrary to those arrived at by Oscar Liebreich. They are as follows:—1. The action of chloral hydrate on similar organisms is different from that of chloroform. 2. This action is peculiar to that body, but it may be considered as the resultant of the two products into which it splits up when placed in contact with the blood, viz., chloroform and formic acid. 3. The action of the hydrate is different from that of trichloracetic acid, and of sodic trichloracetate, which both split up into chloroform and acetic acid. A part of the chloroform formed by the action of the alkaline carbonates of the blood upon the chloral hydrate, is eliminated through the lungs, whilst a part of the formic acid generated is found in the urine.

T. S.

Agricultural Chemistry.

Some Experiments on the Germination of Seeds. By A. VOGEL.†

THE author had shown that kermes, cupric oxide, and other bodies generally regarded as insoluble in water, are capable of hindering germination, if used as a matrix for the seed. It is known that organic acids are produced in germination; the author endeavoured to ascertain the quantity so formed. 100 grams of barley were allowed to germinate, then thoroughly washed; and the solution was boiled and titrated with soda: the acid found was equivalent to ·17 grm. H_2SO_4. Clover and cress seed treated in the same way, but the solutions not boiled, yielded, respectively, acid equivalent to ·35 grm. and ·44 grm. of H_2SO_4. The injurious action of the matrix in the previous experiments was probably due, in many cases, to the solvent action of these organic acids.

Red phosphorus and aniline were found to be especially inimical to germination.

Lea had shown that wheat would germinate in very dilute solutions of various acids, salts, and vegetable bodies; the author repeated these experiments with clover and cress seed, and confirms Lea's results. In a solution of potassium permanganate, germination is not perfect; but seeds moistened repeatedly with a weak solution ($\frac{3}{1000}$), and then

* Comp. rend., lxxii, 742. † N. Repert. Pharm., xx, 132—143.

washed, germinate more quickly than seeds moistened with water. The permanganate here acts like chlorine, bromine, and iodine.

In his later experiments, the author employs thin layers of a highly porous peat as a support for the seeds, the layers being placed in shallow vessels filled with the solutions to be tried. The results obtained by this method with cress and clover seed were as follows:—

Substance dissolved.	Grammes in 1 litre.	Result obtained.
Sulphuric acid	20·00	No germination.
"	4·00	No germination.
"	·80	Half seeds germinated, but imperfectly.
Arsenious acid	·10	No germination, nor when removed and washed.
Arsenic acid	Very dilute.	Germinated when removed and washed.
Hydrocyanic acid	·18	No germination till acid had disappeared.
Oxalic acid	2·10	No germination, nor when removed and washed.
Acetic acid	2·10	Result as above.
Phenylic acid	1 drop in 50 c.c.	No germination.
Bichromate of potassium ..	·50	No germination.
Sulphate of copper.....	1·00	Two-thirds seeds germinated, but imperfectly.
Nitrate of silver.....	·50	No germination.

Impure coal-gas was found to prevent germination. Moist naphthalene used as a seed-bed had no injurious effect.

R. W.

On Humate of Ammonia. By A. VOGEL.*

THE author had previously observed that plants grown on soil rich in silica and poor in humus, contain less silica in their ash than those grown on soil poor in silica but rich in humus. Since an excess of silica is always present in soil, the amount taken up by a plant must clearly depend on other circumstances than the quantity at its disposal. Thénard has recently thrown light on the subject by showing that humic acid forms with ammonia and silica very permanent acid compounds. These compounds are soluble in very dilute alkali, from which solution they can be separated unchanged; they lose nitrogen only at a high temperature. Humic acid does not combine with silica, unless ammonia be present. It appears probable from these observations that humic acid plays an important part in the economy of plant growth.

* N. Repert. Pharm., xx, 113–146.

When seeds germinate on wet blotting-paper, a brown zone, having the reactions of humus, forms at some distance from the seed. The author concludes that humus is produced in this case from a soluble colourless body by the action of the atmosphere.

R. W.

On the Precipitation of Muddy Matter by Weak Saline Solutions. By C. SCHLŒSING.*

THE author had noticed that when a soil is treated with distilled water in a displacement-apparatus, the drainage is at first clear, but that in a later stage of the washing, it generally passes turbid. The turbidity of the water continues, notwithstanding it be left at rest a long time, but the addition of a calcium salt determines the immediate coagulation of the mud, and the water is at once clarified. Experiments were tried with plastic clay. Calcium chloride, $\frac{1}{1000}$ of the liquid, precipitated the suspended matter immediately; $\frac{1}{5000}$ precipitated after some minutes; $\frac{1}{50000}$ clarified in two or three days. Chloride, nitrate, sulphate, bicarbonate, and hydrate of calcium have, apparently, an equal effect. Magnesium salts nearly equal the salts of calcium in this respect. Potassium salts must be used in five times greater quantity than salts of calcium. Sodium salts are still less effective. The precipitation of the clay seems to depend on the strength of the saline solution, and to have no connection with the quantity of clay suspended. On treating the coagulated clay with distilled water, it regains its power of permanent diffusion.†

The author concludes from these facts that the conservation of clay in surface soils is entirely due to the saline matters present, without which the clay would be easily removed by rain. The formation of deltas at the mouths of rivers, and the transparency of the waters of the ocean, he ascribes to the precipitating power of salt water. He recommends that the mechanical analysis of soil should always be performed with distilled water, without which it is impossible to separate clay from very fine sand. When the distilled water with its suspended matter is allowed to rest a long time, the sand deposits, the clay remains suspended. The author suggests the employment of calcium salts to clarify turbid waters intended for the supply of towns, and points out that flood waters which have never penetrated the soil are those which are most obstinately turbid, and are also, of course, those containing least saline matter.

R. W.

* Jr. Pharm. [4], xiii, 107—111.

† These observations have been in great part anticipated by W. Skey; see Chem. News, April 3, 1868.—R. W.

On the Influence of Marl on the Formation of Carbonic Acid and Nitric Acid in Soil. By KARL PETERSEN.*

ABOUT 25 grams of a heavy clay soil, air-dried and reduced to powder, were mixed with pure sand to insure porosity, then moistened, and placed in a glass tube. Air deprived of carbonic acid was then drawn through the soil during 384 hours; the air after leaving the soil was conducted into baryta-water. A comparative experiment was made with the same soil plus carbonate of calcium. The air from the natural soil yielded 14·89 milligrams of CO_2; the air from the marled soil, 42·59 milligrams. Similar experiments were made with leaf-mould, a soil which was strongly acid, and contained 58 per cent. of humus. The natural soil in this case gave 44·67 milligrams of CO_2; the same, plus 1 per cent. carbonate of calcium, 181·12 milligrams; the same, plus 2 per cent. carbonate of calcium, 244·71 milligrams. It appeared, therefore, as might have been expected, that the addition of marl decidedly increased the formation of carbonic acid.

Experiments were tried with two soils, and with a subsoil to which uric acid had been added, in which the moist soils, with or without carbonate of calcium, were kept for several weeks at a temperature of 20° to 25°. The carbonate of calcium did not in any case increase the formation of nitric acid. In a further experiment with leaf-mould, the presence of calcium carbonate appeared to increase the quantity of nitric acid formed.

R. W.

Analytical Chemistry.

A New Method for the Determination of Available Chlorine in Bleaching Powder. By J. B. F. HERRESHOFF.†

THIS process is based upon the fact that when bleaching powder is made to act upon an excess of stannous chloride in strongly acid solution, stannic chloride is formed, at the expense of all available chlorine in the former. The reaction is represented by the following equation:—

$$Ca(ClO)Cl + 2HCl + SnCl_2 = SnCl_4 + CaCl_2 + H_2O.$$

The amount of stannous chloride is afterwards estimated by means of a standard solution of potassium dichromate, and deducted from the amount originally employed:—

* Chem. Centr., 1871, 346. † Chem. News, xxiii, 293.

$$3SnCl_2 + K_2Cr_2O_7 + 14HCl = 3SnCl_4 + 2KCl + Cr_2Cl_6 + 7H_2O.$$

The process is conducted in the following manner:—

13·8738 grams of pure potassium dichromate are dissolved in water, and the solution is diluted to 1 litre. 1·0 c.c. of this solution is equivalent to 0·01 milligram of chlorine. About 30 grams of stannous chloride are dissolved in water, freely acidified with hydrochloric acid, and the solution is likewise diluted to 1 litre. To ascertain the strength of the stannous solution, 10 c.c. are taken with a pipette, diluted with distilled water; and 5 c.c. of hydrochloric acid, a few drops of solution of potassium iodide, and starch paste are added; the standard solution of dichromate is then run in from a burette, until a blue colour is produced by the liberation of iodine. If 20 c.c. of the standard dichromate solution are required, 1 c.c. of the stannous solution will equal 2 c.c. of the former, and also 0·02 milligram of chlorine.

Again, supposing the tin solutions to be of the above strength, 20 c.c. of the now standardised solution are measured as before, diluted with water, and 1 gram of bleaching powder, well triturated with water added, together with 10 or 12 c.c. of hydrochloric acid. The reaction is energetic and complete, and if sufficient amount of hydrochloric acid is introduced, the solution will become perfectly clear.

A few drops of solutions of starch and potassium iodide are now added, and afterwards standard dichromate solution, until the deep blue colour of iodide of starch remains permanent. Supposing 10 c.c. of the latter solution are consumed, then 10 c.c. ÷ 2 = 5 c.c., 20 c.c. —5 c.c. = 15 c.c. As 1 c.c. of the stannous solution equals 0·02 Cl. and 15 c.c. are required for 1 gram of bleaching powder, then 15 × 0·02 Cl. = 0·030 Cl = 30 per cent.

The author objects to Penot's well known arsenic method, upon the ground that in the first place it is difficult to ascertain the purity of the arsenious acid employed; and secondly, that the solution of sodium arsenite will not remain with certainty unchanged for any length of time. In the present instance, although the tin solution alters slowly by keeping, it is nevertheless a matter of a few moments only accurately to re-standardise it by means of the dichromate solution.

The process, however, is not free from an objection which is sometimes urged against Bunsen's method, viz., that many specimens of bleaching powder contain chlorate, which, liberating chlorine on the addition of hydrochloric acid, will consume a certain volume of standard solution, and thus raise the percentage. Penot's method is not liable to this source of error.

J. W.

The Uselessness of Ammonio-Ferrous Sulphate for the Estimation of Chlorine. By E. BILTZ.*

25 c.c. of chlorine, 0·428 per cent., added to a solution containing 1 grm. of the above double salt, did not oxidise the whole of the ferrous sulphate. On adding, however, the same amount of chlorine to an equivalent quantity of ferrous salt, an excess of that element was found.

A sample of chloride of lime titrated with ferrous sulphate, appeared to contain 32·203 per cent. of chlorine; whereas the double salt gave only 26·813 per cent. The oxidizing power of chlorine on the double salt is also affected by the amount of water present. The difference in the behaviour of chlorine with the two salts is ascribed to its known action on ammonia solutions.

A. T.

Contribution to the Titration of Phosphoric Acid by Uranium Solution. By W. JANI.†

A LARGE number of experiments are described, showing the influence of ammonium salts, acetic acid, and acetates, on this process.

Ammonium salts have no influence. An excess of acetic acid, or an acetate, however, seriously affects the result. To prevent the presence of the latter substances in the solution, the free acid should not be neutralised by sodium acetate, but by adding ammonia or soda carefully, until the solution is slightly alkaline, then a few drops of acetic acid. With this precaution, the results obtained by titration agree with those of the usual methods.

A. T.

On the Estimation of Nitric Acid. By A. WAGNER.

THIS method is based upon the ignition of nitrates, *out of contact with air*, with excess of chromic oxide and sodic carbonate. The change takes place according to the equation:—

$$Cr_2O_3 + N_2O_5 = 2CrO_3 + N_2O_2.$$

The author employs tubes of hard glass, about 10 centimetres long and 7 mm. wide, such as are used in Marsh's apparatus. One end is drawn out and connected, by means of a small india-rubber tube, with a carbonic acid apparatus; the other is cut off smooth, and fitted with

* Arch. Pharm. [2], 97. † Chem. Centr., 1871, 329—333.

a cork and narrow glass tube, bent at right angles, and made to dip under water. A mixture of 3 to 4 grms. of nitre with about 3 grms. of chromic oxide (ignited), and 1 grm. of sodic carbonate is introduced into the tube; the air is completely displaced by a current of carbonic anhydride, and heat is applied to the substance during eight or ten minutes, whilst a slow current of gas is kept up to carry off the nitric oxide gas. The tube is allowed to cool in a current of carbonic anhydride. Its contents are dissolved out with warm water, filtered, and the chromic acid is determined, according to Rose's method, by *slightly* acidulating the alkaline solution with nitric acid, heating gently, and precipitating with mercurous nitrate. The precipitated mercurous chromate is collected on a filter, washed with a dilute solution of mercurous nitrate, dried, and cautiously ignited in a covered crucible, when mercury vapour and oxygen escape. The heat is then raised, and the chromic oxide strongly ignited and weighed, till constant. One part by weight of the oxide corresponds to ·7068 part of nitric anhydride. The author remarks that the proportion of sodic carbonate to chromic oxide (1 : 3) should not be exceeded, in order to guard against fusion, and that the presence of organic matter detracts greatly from the accuracy of the method.

The quantitative results adduced by the author are satisfactory. He appears, however, to have confined himself to the estimation of nitric acid in commercial saltpetre, for which, as is well known, several simpler, yet equally accurate methods already exist.

W. V.

On the Quantitative Estimation of Organic Matter and Nitric Acid in Potable Waters. By G. C. WITTSTEIN.*

ON igniting the saline residue left by evaporating potable waters (which almost invariably contain more or less nitric acid, in the form of nitrates of calcium, magnesium, &c.), even after previous treatment with excess of sodic carbonate, extracting with hot water, and filtering, a more or less considerable loss is incurred, owing to the oxidation of the organic matter by the nitrates present, and consequently the partial or complete destruction of the latter, with formation of nitrites or carbonates. The author proposes to correct this error by cautiously neutralising the alkaline residue with dilute nitric acid, in order to replace the loss incurred on ignition. The neutralised residue is again evaporated to dryness; a weighed quantity of finely powdered quartz (about one-third of the latter to the total quantity of saline residue) is added, and the mass desiccated at 120°, and weighed till constant.

* Dingl. Polyt. Journ., cc, 123.

The residue is ignited for a quarter of an hour, and weighed again. This second loss represents the total nitric acid originally present in the water, and by deducting the total weight of the ignited saline residue and quartz powder, dried at 120°, previous to ignition, plus the weight of the quartz powder, the author arrives at a knowledge of the organic matter present in the saline residue.

W. V.

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*Volumetric Estimation of Zinc.**

THE author records his experience of the substitution of cobaltous chloride, first proposed by A. Deus,† as an indicator of the completion of the precipitation of zinc by means of sodium sulphide, instead of ferric chloride, lead-solution, nickel chloride, or sodium nitroprusside. He prepares a standard solution of sodium sulphide by dissolving 40 to 50 grms. of the crystallised sulphide in 400—500 c.c. of water, or by dividing ordinary caustic soda into two parts, saturating the one completely with sulphuretted hydrogen, adding the other to it, and diluting the whole with four volumes of water. The solution of zinc required for determining the titre of the sodium sulphide is prepared by dissolving 2 to 3 grms. of pure zinc or of zinc oxide in hydrochloric acid, and diluting with 200 to 300 c.c. of water. The preparation of the cobalt paper is best effected by precipitating cobaltous hydrate from a cobaltous solution by means of sodium carbonate. ·35 grm. of the ignited oxide are dissolved in hydrochloric acid; the excess of acid is removed by cautious evaporation, and the residue dissolved in 100 c.c. of water. Strips of filter paper, 2 to 3 inches wide, are passed through this solution, and dried at the ordinary temperature or at a gentle heat, in which case the paper becomes locally blue, which colour however disappears on cooling.

The end of the reaction of the sodium sulphide upon the zinc solution is ascertained by dipping a glass-rod into the solution and transferring a small drop on the cobalt paper. As long as any zinc remains to be precipitated, the drop leaves either no mark at all, or only a faintly blue wet spot, which disappears completely on drying. It is, however, not necessary to await the drying up of the spot, or at all events only when the experiment is tried for the first time. As soon as the whole of the zinc is precipitated, the least excess of sodium sulphide produces on the cobalt paper a slight, yet *unmistakable* change of colour. Instead of appearing pale blue, the spot shows a decidedly green tint, passing

* Oest. Zeitschr. f. Berg und Hüttenwesen, 1871, No. 16. Dingl. polyt. J., cc, 217.

† Fres. Zeitschr. für anal. Chem., 1870, iv, 465.

rapidly to a light brown, especially on holding the paper over a warm sand-bath.

Zinc ores which contain iron should be repeatedly precipitated with ammonium chloride and ammonia, and redissolved in hydrochloric acid as long as any zinc oxide remains with the ferric hydrate. Lead or copper, or both, when present in ores of zinc, are removed by sulphuretted hydrogen. The solution of sodium sulphide should be standardised freshly every two or three days.

W. P.

The Estimation of Manganese in Spiegeleisen and Ferro-Manganese. By THOS. ROWAN.*

UNDER the above title, the author details the results of his experience respecting the quantitative separation of iron and manganese by means of sodic acetate: he claims no originality in the practical working of the process, but having frequently employed it, recommends it as a speedy, accurate, and trustworthy method. About $1\frac{1}{2}$ grams of the sample, in a fine state of division, are digested with 100 c.c. of hydrochloric acid until complete solution is effected; a small quantity of potassic chlorate is then added to peroxidise the iron, and the whole is gently evaporated to a small bulk, to remove the last traces of chlorine, and any large excess of hydrochloric acid. The solution is next neutralised with sodium carbonate, diluted with about 200 c.c. of distilled water, and the iron precipitated as basic salt, by the addition of a concentrated solution of sodium acetate. The flask and its contents are briskly boiled for twenty minutes, allowed to repose for a short time, and the clear solution is poured upon a filter. More water is then added to the flask, together with a few drops of sodium acetate, the solution boiled for five or six minutes, and again decanted from the precipitate. This operation is repeated a third time, after which the ferric acetate may be collected on the filter, and washed with boiling water.

The filtrate containing the whole of the manganese originally present in the sample, is brought to a temperature of about 40°, and a stream of chlorine gas passed through, until a faint smell of that gas can be detected in the liquid; the beaker is then carefully covered, and set aside in a moderately warm place for six hours.

By this treatment the manganese is brought to a higher state of oxidation, and simultaneously precipitated as peroxide; a trace of permanganic acid is often formed, which communicates to the liquid a

* Chem. News, xxiii, 279.

purple tinge; this may be reduced by the addition of a few drops of alcohol, and the whole of the precipitated manganese filtered off.

Owing to the tendency of the peroxide to appropriate alkali, it cannot be directly reduced by ignition to the red oxide; it is therefore dissolved in warm hydrochloric acid, and re-precipitated as carbonate by a solution of sodium carbonate; the precipitate is collected on a filter, well washed with boiling water, dried, ignited, and weighed as the red oxide. 100 parts of Mn_3O_4 contain 72·05 parts of metallic manganese.

J. W.

On the Use of Potassium Ferricyanide as a Test for Cobalt, Nickel, and Manganese. By ALFRED H. ALLEN.*

IF to a solution of a salt of cobalt there be added ammonium chloride, ammonia, and excess of potassium ferricyanide, the liquid immediately assumes a deep blood-red coloration, similar in appearance to the reaction between potassium sulphocyanate and a ferric salt: the solution remains perfectly clear, even on heating, and no precipitation whatever of the cobalt takes place.

On the contrary, if a salt of nickel in similar solution be substituted for the cobalt, and the solution gently boiled, the liquid first becomes turbid, and in a short time deposits the whole of the nickel as a copper-red precipitate, which has a great tendency to adhere to the sides of the vessel. The presence of cobalt in no way interferes with the precipitation of the nickel, neither does this latter metal obscure the coloration produced by the cobalt: we have therefore in the foregoing test, a ready means of detecting these two metals, when they occur together in the same solution.

The author has partially examined the red precipitate of nickel, and finds that it does not contain sufficient nickel to correspond either to the formula $Ni_2(C_6N_6Fe)$ or to $Ni_3(C_6N_6Fe)_2$, it also evolves ammonia when acted upon by caustic soda.

When a solution of manganous sulphate is treated with ammonium chloride and ammonia, and potassium ferricyanide gradually added, a whitish precipitate is first formed, which changes on the addition of more ferricyanide, to a dark brown colour. As this reaction takes place immediately in the cold, it may serve to distinguish manganese from cobalt and nickel; but unfortunately the manganese interferes with the subsequent tests for cobalt and nickel, when all three metals are present in the same solution.

* Chem. News, xxiii, 290.

An ammoniacal solution of zinc sulphate, in presence of ammonium chloride, is not precipitated, either in the cold or on boiling, by the addition of potassium ferricyanide; but potassium ferrocyanide instantly throws down the zinc as a white precipitate. Since the four metals, nickel, cobalt, manganese, and zinc, frequently occur in analysis in presence of ammoniacal salts, the author proposes the above method as a means of distinguishing them from each other. One of the following reactions taking place:—

(1.) A brown precipitate: manganese.

(2.) A deep red solution: cobalt.

(3.) No change in the cold: a copper-red precipitate on boiling indicates nickel.

(4.) No change in either hot or cold liquid; add potassium ferrocyanide: a white precipitate indicates zinc. J. W.

The Determination of Copper in Brass by Titration.
By M. Kirpitschon.*

In the titration of copper by potassium cyanide or sodium sulphide, more of these substances is required than corresponds to the amount of copper present in the brass. The author has experimented on the influence of certain substances and of heat on the operation, with the following results:—

1 grm. of ammonium sesquicarbonate requires an extra quantity of KCy equal to ·00042 grm. of copper; 1 grm. of ammonium sulphate ·00092; and 1 grm. of ammonium nitrate ·00082 copper.

The higher the temperature, the smaller was the extra quantity of potassium cyanide required. The greater the quantity of zinc, the less accurate were the results.

In titrating an ammoniacal solution of zinc and copper with sodium sulphide, somewhat more of this substance was used than pure copper required; but this excess, amounting to about $1\frac{1}{2}$ per cent., was a constant quantity. A. T.

On the Determination of Molybdic Acid as Plumbic Molybdate.
By Thomas M. Chatard.†

The author proposes the following method as being more accurate and easier of execution than the ordinary methods of precipitation of molybdenum as sulphide or as mercurous molybdate. He mixes the boiling solution of the molybdate with plumbic acetate in slight excess, and boils the liquid for a few minutes; the precipitate, at

* Zeitsch. f. Chem. [2], vii, 207—209. † Am. Journ. Sci. [3], i, 416.

first milky, becomes granular, and subsides easily, leaving a perfectly clear supernatant liquid. Care must be taken in boiling, as the thick milky fluid is very apt to boil over. The liquid is then filtered through a ribbed filter, the precipitate washed with hot water, dried at 100°, removed from the filter, and lastly ignited in a porcelain crucible.

The results obtained by the author were as follows:—

1·0744 grm.	Na_2MoO_4	gave	1·9176 grm.	$PbMoO_4$	=	46·64	per cent.	Mo.
1·4440 „	„	„	2·5738 „	„	=	46·60	„	„
1·2221 „	„	„	2.1811 „	„	=	46·66	„	„
1·2871 „	„	„	2·2999 „	„	=	46·74	„	„

Mean 46·66.

The theoretical percentage of Mo in Na_2MoO_4 is 46·60, if Mo be taken as = 96, according to the most recent determinations.

The method is easy and expeditious. The precipitated molybdate separates easily from the filter, and can be heated to low redness without decomposition.

C. G.

Examination for Arsenic, Antimony, Phosphorus, Phosphorous Acid, and Sulphurous Acid. By — HAGER.*

THE author recommends his method for the rapid testing of officinal phosphoric, hydrochloric, and sulphuric acids. The substance, dissolved in water, is mixed with dilute sulphuric acid; pure zinc is added; and the escaping hydrogen allowed to pass over the surfaces of strips of parchment-paper moistened with silver nitrate, copper sulphate, and lead acetate respectively. Blackening of these strips indicates the formation of gaseous hydrogen compounds. Phosphoretted hydrogen blackens the copper salt, but not either of the others. Arsenetted and antimoniuretted hydrogen blacken the silver and copper salts, but not the lead, while sulphuretted hydrogen blackens all three.

C. H. G.

On Spectrum Analysis applied to the Quantitative Determination of Colouring Matters. By K. VIERORDT.†

IN his former‡ preliminary note on this subject, the author did not enter into a number of more or less important secondary conditions, not to be disregarded in such investigations. Anticipating possible misconception, he now calls attention to the following point. The relation between the concentration (C) of the solution and its coefficient of

* Chem. Centr., 1871, 384. † Deut. Chem. Ges. Ber., iv, 519.
‡ Page 602 of this volume.

extinction of light (E) remains constant only within certain limits of variation in concentration. If in the determination of a colouring matter it be not desired to determine the relation $\frac{C}{E}$ for concentrations 4—6 apart, the value $\frac{C}{E}$ for a single strongly diluted solution ("test solution") of the colouring matter may be estimated. Every solution of unknown strength of the colouring matter in question has then to be diluted until its absorptive action on a certain region of the spectrum about coincides with the absorptive action of the test solution. The absorption-coefficient (A) of the test-solution is then equal to the absorption-coefficient of the solution under examination, and the formula $C = AE$ serves for the calculation of the unknown value C.

H. E. A.

On the Quantitative Determination of Colouring Matters by Means of the Spectroscope. By HUGO SCHIFF.*

MANY coloured solutions, when examined by the spectroscope, show at a certain degree of concentration, absorption-bands which disappear again on further dilution. The following solutions were examined at the mean temperature, the layer of liquid having a thickness of one centimetre:

Rosaniline acetate (1 : 45,000) gives a well-defined dark band between D or E; on further dilution (1 : 80,000) another narrower band appears at F. The first band becomes very faint at 1 : 200,000, but the last traces disappear only at 1 : 1,000,000. Rosaniline nitrate shows the band between D and E at 1 : 20,000, and it can be observed until the dilution is 1 : 400,000. Insoluble aniline-blue gives, at 1 : 25,000, an absorption band which extinguishes the whole of the yellow; at 1 : 15,000 it becomes very narrow, and disappears at about 1 : 300,000. Cyanine (chinoline blue) gives, at 1 : 12,000, a dark band between D and E, the last traces of which disappear at 1 : 500,000.

From the observations of Valentin, the author calculates that the absorption-spectrum of blood disappears at 1 : 1,100,000.

To analyse a colouring matter by this method, 1 gram is dissolved in one litre, and this solution is further diluted until it gives the same spectrum as a solution of known strength of the pure compound exhibits under the same circumstances. Most of these solutions show, in a thickness of one centimetre, a faint but distinct colour, even when the spectrum disappears; but the reaction of blood can be distinctly observed when the solution is quite colourless.

C. S.

* Deut. Chem. Ges. Ber., iv, 474—475.

Valuation of Chloral Hydrate. By F. VERSMANN.*

THE author, who, some time ago, proposed sulphuric acid instead of ammonia for testing the value of chloral hydrate, now states that in working upon 10 grams of chloral hydrate, there is a constant loss by the ammonia test of 0·2 c.c. of chloroform, owing to the solubility of the latter in water; and that if the necessary correction be made, the result corresponds with that obtained by the sulphuric acid test. The latter test, however, is recommended as preferable, on account of the shorter time required for the experiment. In four samples from different manufacturers, the percentage of chloral hydrate was found to vary from 90·80 to 96·99 per cent. by the ammonia test, and from 91·18 to 97·09 per cent. by the sulphuric acid test. J. B.

Detection of Turmeric in powdered Rhubarb and Yellow Mustard. By J. M. MAISCH.†

INFERIOR rhubarb is often adulterated with powdered turmeric in order to improve its colour. The fraud may be detected in a few minutes in the following manner:—

A small quantity of the suspected rhubarb is agitated for a minute or two with strong alcohol and filtered. A strong solution of borax is then added to the filtrate, and afterwards a considerable excess of hydrochloric acid. If the rhubarb be pure, the tincture itself will possess a light brown tint, and the red-brown colour produced by the borax will be instantly discharged by the action of the hydrochloric acid. If, on the contrary, the sample be adulterated, the tincture will be of a brighter yellow than in the previous instance, and the brown colour will, after the addition of the acid, either remain persistent or change merely to a lighter shade of red.

The same test, applied in the same manner, is also applicable to ground mustard-seed. On agitation with alcohol and filtering, a turbid solution is obtained, which assumes a bright yellow on the addition of the borax solution, and becomes colourless, or whitish again, on being supersaturated with hydrochloric acid. If the mustard be coloured with turmeric, the filtrate has a yellow tint, and the red colour communicated by the borax remains persistent, as in the previous instance.

J. W.

The Estimation of the Value of Oil Seeds. By Dr. VOHL.

A DESCRIPTION, accompanied by a drawing, is given of an apparatus for effecting the above. It consists of an extractor, head, cooler, and

* Pharm. J. Trans. [3], i, 965. † Pharm. J. Trans. [3], i, 1027.

boiler made of glass. The solvent is poured on the seed in the extractor, through which it descends to the boiler. The oily solution obtained is then heated and the vapour of the solvent ascends, by a pipe, through the centre, to the top of the extractor, where it is condensed by the head and cooler and may be used over again.

A. T.

Examination of Sugar after treatment with Sulphurous Acid. By P. SCHULZE.

THE plan of treating raw sugar with sulphurous acid gas whilst being evaporated *in vacuo* is known as Dr. Seyfertt's process. It was thought that the sugar so prepared would contain an excess of sulphuric acid, and in consequence deteriorate the animal charcoal. The author therefore examined a number of samples prepared by the sulphurous and other processes, but failed to notice any marked difference in this respect. He then treated Seyfertt's sugar with aluminium in an acid solution; sulphuretted hydrogen was evolved, the quantity of which could not be ascertained, but was believed not to exceed 0·03 per cent. Volatile organic acids are said to be expelled. The carbonates in the ashes of sulphurous and other sugars were estimated. The quantity found did not indicate any notable difference. The author concludes from this that either the syrup was free from volatile organic acids or that the gas did not expel them.

A. T.

Methods of Analysis, and Composition of various Manufacturing Products: Palm-oil, White Lead, Zinc-white, Water used for feeding Boilers. By GASTON TISSANDIER. (Chem. News, xxiii, 269.)

Note on the Analysis of Molasses. By A. VIVIEN. (Chem. News, xxiii, 281.)

Note on the Analysis of Chrome-iron Ore. By E. STODDART. (Chem. News, xxiii, 284.)

Critique on the Analytical Methods employed in estimating the Tannin contained in Catechu and some other Drugs. By GÜNTHER. (Chem. Centr. 1871, 395—397.)

Technical Chemistry.

On the Contamination of Iodine with Iodine Cyanide.
By G. C. Wittstein.*

Dr. Wittstein obtained a sample of iodine containing much iodine cyanide, distributed throughout its mass in the form of white needles. By rubbing a weighed quantity with an excess of mercury, washing out the iodine cyanide and weighing the residue of mercury and mercurous iodide, it was found that the sample contained 28·75 per cent. of the iodine cyanide.

On endeavouring to remove the impurity by sublimation (on the large scale), so much iodine was found to accompany the cyanide that the attempt was abandoned. The sublimate contained 56·8 per cent. iodine cyanide. Herzog (Archiv. der Pharm. lxi, 129) has shown that iodine containing iodine cyanide, when treated with iron and water, gives a liquid containing both iodide and cyanide of iron, but that when this is acted on by potassium carbonate the whole of the cyanogen is precipitated, and that therefore the potassium iodide so prepared is free from potassium cyanide.

C. H. G.

The Use of Animal Charcoal for the decolorisation of Sugar Solutions in Polarimetrical Analysis.

Dr. Sheibler, in the "Zeitschrift des Vereines für die Rüben Zucker-Industrie," vol. xx, 218, showed that even so little as five grams of animal charcoal can absorb enough sugar from 50 c.c. of normal strength, to reduce the observed percentage by as much as 0·5 per cent., and that by doubling the quantity of bone-black a double quantity of sugar is absorbed from solution. Dr. Scheibler's numbers were reproduced in the Pharm. J. and Trans. [2], i, 926.

C. H. G.

Note on the Use of Gaize for the Preparation of Alkaline Silicates.
By Aug. Scheurer Kestner.†

The object of the author was to determine whether the above rock could be used for the manufacture of solution of silicate of soda without fusing with an alkali. The sample with which he experimented had the following composition:—

* Dingl. polyt. J., cc, 310. † Compt. rend., lxxii, 767—769.

Hygrometric moisture	3·4
Combined water	3·2
Soluble silica	43·7
Insoluble silica	40·8
Alumina	3·8
Ferric oxide	2·9
Lime	0·9
	98·7

On boiling 600 grams with 750 grams of a solution of caustic soda, sp. gr. 1·12, a brown liquor was obtained. To avoid this colour, the rock was calcined, which did not diminish the solubility of the silica. On boiling the calcined rock with caustic soda, sp. gr. 1·25, for half an hour, a solution was obtained which furnished a dry silicate containing silica 68·7 per cent., sodium oxide 31·3 per cent. On boiling for a longer time, a silicate was obtained containing silica 67·98 per cent., sodium oxide 24·00 per cent.

The author endeavoured to increase the solubility by pressure, but without avail, the resulting silicate containing 69·51 per cent. silica, and 30·49 per cent. sodium oxide. He concludes that gaize is not a suitable material for preparing commercial alkaline silicates by the wet way. Commercial silicate of soda of good quality contains silica 76 per cent., sodic oxide 24 per cent.

Note by the Abstractor.—Gaize is a rock found underlying the cretaceous strata. It is known in the department of Ardennes under the names of *gaize* or *pierre-morte*.

E. T. C.

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*Uses of Infusorial Silica.**

THE large deposits of diatomaceous earth so abundantly distributed in various parts of the globe, have already received the following important applications in the arts:—1. As a substitute for heavy spar in the manufacture of india-rubber goods, when it is required that the article shall be of sufficient density to sink in water.—2. By mixing 3 to 6 parts of this infusorial silica with 1 part of freshly burnt lime, and stamping the whole, after slightly moistening with water, into a suitable mould, an impervious artificial stove of any desired form can be made. A cement known as "albolith" is now

* Chem. News, xxiii, 279.

produced in Germany, by combining infusorial earth with magnesite and magnesium chloride, the latter being obtained as an incidental product in the salt manufacture.—3. A fine glaze for earthenware is obtained by fusing infusorial earth with crude calcium borate (boronatrocalcite). If magnesium borate be substituted for calcium borate, a peculiar variety of porcelain is formed, capable of being blown almost as readily as glass.—4. Infusorial silica is now employed for absorbing nitro-glycerin in the manufacture of dynamite, and it is also probable that, owing to the ready solubility of this form of silica in caustic soda, it will ere long receive an application in the preparation of soluble glass.

J. W.

Prevention of Injury from the Presence of Lime in Brick Clay. By R. Hurschberg.*

The heat employed in burning bricks is not sufficient to burn the lime "dead:" consequently any lumps of that body which are left in the clay gradually slake, swell, and cause the bricks to crumble. The author proposes to get over this difficulty by mixing the clay, not with water, but with a saturated solution of borax. His experiments show that this method can be successfully carried out if the cost does not debar its employment.

C. H. G.

On the Absorption of Sulphur by Gold, and its Effects in Retarding Amalgamation. By W. Skey.†

It has been long noticed that a considerable loss of gold is always experienced in working auriferous material by the amalgamation process, which can scarcely be referred to any of the causes generally supposed to be operative.

A careful investigation respecting the nature of the above-mentioned loss has elicited the fact that, although a sample of gold may present a bright stainless surface, and be to all appearance chemically clean, yet it not unfrequently happens that such sample will absolutely refuse to amalgamate with mercury; and since the extraction of the gold depends upon the success of the amalgamation, it is obvious that, if amalgamation does not take place, an undoubted loss of metal must ensue.

Pursuing the enquiry, it was found that all such specimens were rendered capable of amalgamation, by immersion either in nitric acid

* Arch. Pharm. [2], cxlvi, 196—199. † Chem. News, xxiii, 277.

or in cold solutions of chromic acid, potassium cyanide, &c.; and also (excepting the more cupreous alloys) by roasting them for a short time in an open fire.

It was suspected that sulphur was present in the gold, forming possibly a thin film of sulphide upon the surface of the metal; that this film prevented direct contact with the mercury; and further, that the roasting, &c., volatilised or destroyed the sulphur, and thus presenting fresh surfaces, rendered them again capable of amalgamation.

To test the truth of this assumption, the surfaces of several samples of pure gold were well cleaned, then immersed for a few seconds in sulphuretted hydrogen gas, and, after washing, dipped beneath the surface of clean mercury; as was anticipated, no amalgamation whatever took place. The same phenomenon was observed when alkaline sulphides were substituted for the sulphuretted hydrogen; also when samples of gold were kept a short time in boiling water, in contact with sulphur.

As in the case of the first series of specimens, they were rendered capable of entering into union with mercury, either by the application of heat, or by treatment with solutions of potassium cyanide, nitric acid, or chloride of lime.

As a proof that gold, thus treated with sulphuretted hydrogen or alkaline sulphides, and afterwards thoroughly washed, does really contain sulphur, although no visible change is induced in its appearance, the solution of potassium cyanide, in which it was subsequently immersed, gave a good reaction of sulphur, when tested with nitro-prusside of sodium.

It is assumed that this absorption is a purely chemical, and not a mechanical action, inasmuch as it was found impossible to remove free sulphur by treating the gold with ether or carbon disulphide; or to demonstrate the presence of sulphuretted hydrogen by the well known reaction with sulphurous acid: whether these experiments be conclusive or not, it is certainly more probable to assume, that upon the exterior of the gold, the sulphur and metal are in a state of chemical combination.

In whatever form, however, sulphur is thus absorbed by gold, it is certainly the greatest obstacle to thorough and complete amalgamation, which has to be contended with. The remedy which naturally presents itself is to employ sodium-amalgam instead of mercury, as first suggested by Mr. Crookes; its effect in relation to the sulphide would be to decompose it, and so expose the encrusted gold to the action of the mercury.

In conclusion, the author hazards the opinion, that, inasmuch as the present evidence tends to show that sulphide of gold is very easily and rapidly formed, it seems probable that sulphur plays a very

important part in the solution and deposition of native gold; that it may effect the translation of this metal from rock-masses to intersecting quartz reefs, and possibly even from deep strata to more superficial positions.

J. W.

On the Silvering of Gelatin Relief-forms for Galvanoplastic Work. By H. HANISCH.*

As graphite, silver sulphide, or precipitated silver, when strewed on a matrix in relief, will not give a continuous easily conducting surface, they cannot be used for fine work. Herr Hanisch therefore proposes to deposit metallic silver on the surface of the gelatin by the action of sunlight. The gelatin leaves are first fixed to a glass plate by copal varnish, next laid in a concentrated solution of tannin for an hour to render them insoluble, and then immediately plunged into a solution of silver nitrate so that their whole surface is covered. A copper wire bent to a right angle is now to be drawn over the surface of the forms while exposed to sunlight: this causes silver to be deposited on those portions touched by the copper; the plate is now to be withdrawn from the solution and exposed to sunlight till dry, after removal of excess of silver by washing it is ready for use.

C. H. G.

Waterproofing Linen and Cotton Cloth. By W. GRÜNE.†

THE fabric is saturated with a solution of gum or gelatin containing $\frac{1}{10}$—$\frac{1}{50}$ of bichromate of potash and then exposed to sunlight. The gelatin becomes insoluble and firmly fixed to the cloth.

C. H. G.

On the Waterproofing of Linen. By A. KUHR.‡

THE material is passed through; first a bath of neutral sulphate of alumina dissolved in two parts of cold water; secondly, through a soap-bath prepared thus: 1 part good resin is dissolved in 10 parts boiling water by help of 1 part crystallised soda, and the soap so produced is salted out, and dissolved in 30 parts of boiling water together with 1 part of white curd soap. The mixture of resin and fat soap gives rise to the formation on the cloth of an alum soap of the best consistency, which is wetted with difficulty.

C. H. G.

* Dingl. Polyt. J., cc, 314. † Ibid., 339. ‡ Ibid., 340.

Application of Straw to Paper-making. By F. G. HAHN. (Dingl. Polyt. J. cc, 321.)

On Peru Gum in regard to its applicability as Thickening Material for Printing. By E. and A. DOLLFUS.*

THE so-called Peru gum is the root of a kind of asphodel, one of the Liliacæ, which is powdered in a particular manner and sifted so as to separate as much as possible of the outer rind and the inner woody portions. The powder so obtained is brownish, very slightly soluble in cold water, in which, however, it swells up enormously; with boiling water it forms a slime, like that of tragacanth, only darker coloured and more binding. This slime contains at least 30 per cent. of insoluble woody matter, which cannot be removed by passing through a sieve, and in practice rapidly fouls the rollers.

The conclusions of the authors are that this material cannot be advantageously used, except for printing broad stripes, and then only with particular colouring bodies. When gently roasted, it gets somewhat darker in colour, but is otherwise improved as a thickening material, but still resists attempts to separate from it those insoluble portions which smear the rollers.

C. H. G.

Recovery of Colouring Matter and Oxalic Acid from the Wash-waters of Madder in Garancin Making. By PERNOD.†

GARANCIN is prepared by boiling powdered madder with dilute sulphuric acid and then washing the residue to remove soluble constituents. The wash-waters are allowed to run to waste in the rivers, though they contain some colouring matter and oxalic acid, besides bodies which rapidly undergo a stinking putrefaction.

M. Pernod finds that by neutralising these wash-waters with lime and allowing them to settle, they are so far purified that they may be allowed to enter the streams without danger to the public health. After neutralisation, the liquid is left at rest for two hours and the clear liquid run away, leaving the precipitate formed by the lime at the bottom of the cistern.

This precipitate, which contains colouring matter, oxalates of lime, and other bodies, is treated with a large quantity of water acidulated with hydrochloric or sulphuric acid (the first wash-waters from the garancin-making) in sufficient quantity to leave the whole mass per-

* Dingl. Polyt., cc, 318—320, from the Bulletin de la Société Industrielle de Mulhouse, xl, 375.

† Dingl. Polyt. J., cc, 315—317, from Bulletin de la Société Industrielle de Mulhouse, xl, 414.

ceptibly acid. The remaining precipitate is collected on a woollen filter and boiled with sufficient sulphuric acid to liberate the whole of the oxalic acid, then after cooling and dilution, it is thrown on a woollen filter and allowed to drain. The filtrate is concentrated in leaden vessels and cooled, when an abundant crop of crystals of oxalic acid is obtained. The pasty mass left on the filter, consisting of calcium sulphate and colouring matter, is repeatedly treated with hot acidulated water to remove the former. The remaining brown mass is somewhat richer in colouring matter than madder, and gives good bright tints, which stand soap, &c., at least as well as madder colours.

C. H. G.

On Böttger's Disinfecting Dressing for Stinking Wounds.

GUN-COTTON saturated with permanganate of potash has been applied to the dressing of foul wounds with happy results. The distressing odour is almost got rid of, and the washing of bandages, &c., is not productive of the usual nuisance. C. H. G.

On Nitroglycerin and Various Dynamites. By GIRARD, MILLOT, and VOGT.*

NITROGLYCERIN is made by treating glycerin of 30° (Beaumé) with six times its weight of a mixture of 1 pt. nitric acid of 48°—50°, and 2 pts. sulphuric acid of 66°. The glycerin is added drop by drop, with constant agitation, to the mixed acids cooled to 10°, care being taken that the temperature does not rise above 25°. When the whole of the glycerin has been added, the mixture is poured into 6 times its weight of water. The nitroglycerin is precipitated as a slightly opalescent syrupy liquid, which is washed twice with water, then with an alkaline solution, and again with water. 100 pts. glycerin gave 130 pts. nitroglycerin. The return may be increased by augmenting the quantity of nitric acid; thus 3 pts. nitric acid, 3 pts. sulphuric acid, and 1 pt. glycerin gave 1·75 p. nitroglycerin of sp. gr. 1·6 at 13°, equal to five-sevenths of the theoretical return. The product must be dried with potassium carbonate, as calcium chloride produces an evolution of chlorine. It does not crystallise at —20°.

Industrial preparation. The different sheds should be separated about 50 yards from each other. They are circular, open at the sides, and have a light roof covered with bitumenised paper; the boards of the floor are inclined downwards from the centre; a constant flow of water removes any nitroglycerin that might otherwise accumulate on the ground. About the centre post are arranged six water troughs, in

* Moniteur Scientifique, xiii, 58—60.

which are placed cylinders of glass, stoneware, or cast-iron; the cylinders are surmounted by channels filled with water, which makes a water-joint between the cylinders and their covers; the latter have several tubulures through which pass: 1. a tube passing to the bottom of the cylinders and conducting air into the mixture for the purpose of maintaining a constant circular motion; 2. a tube furnished with a tap by which the flow of glycerin is regulated; 3. a large tube acting as a chimney to carry off vapours which would otherwise occasion violent headaches; 4. a thermometer. Levers fixed to the side of the troughs enable the workman to depress the cylinders into the water and to empty them into the troughs, which are furnished with several openings closed with plugs to facilitate the decantation and washing of the product. The washing is effected in the troughs by a water pipe fitted with a rose jet. One workman can superintend six troughs. 500 grams of glycerin are used in each operation.

Dynamite. The experiments on the relative explosibility of various kinds of dynamite were made with a weight of 4 kils., 700 falling between guides on a space of 2 square centimetres upon an anvil. The sample of dynamite experimented on was wrapped in paper. With this arrangement sporting powder did not explode.

The authors' results show that—1. The best materials to be added to nitroglycerin are tripoli, kaolin, silica, alumina, and especially sugar, which has the additional advantage of being, in case of necessity, easily separated from the nitroglycerin by water.

2. In each kind of dynamite, variations in the proportion of the inert substance do not affect the stability of the mixture.

3. Dynamite seems to lose nitroglycerin by long exposure to the atmosphere, and to become inactive.

The authors conclude with statements of many results obtained by them with the above-mentioned apparatus, amongst which occur the following:—

Nitroglycerin explodes at 0·25m.						
,,	1 pt. wood spirit	3 pts.	does not explode	at	1·65m.	
,,	3 pts. glycerin	1 pt.	explodes with difficulty	at	1·65m.	
,,	1 pt. silica	3 pts.	explodes even at 0·5m, with difficulty at 1·65m.			
,,	3 pts. ,,	3 pts.	,,	,,	easily at	1·65m.
,,	3·6 pts. ,,	0·4 pt.	,,	,,	strongly	,,
,,	1 pt. sugar	0·5 pt.	scarcely explodes	at	1m.	
,,	1 pt. ,,	1 pt.	,,	,,	,,	
,,	2 pts. ,,	in lumps	1 pt. scarcely explodes	at	1·65m.	
,,	2 pts. ,,	,,	3 pts. does not explode	at	1·65m.	

F. H. H.

On Dynamite and its Use in War. By P. CHAMPION.*

DYNAMITE differs notably from gunpowder in the manner of its explosion; for whilst the latter does not develop its maximum explosive effect unless it be fired in closed vessels, the far greater explosive power of dynamite is manifested, even though it be fired in contact with any solid resistance in the open air.

Preparation.—The most appropriate substance for mixing with nitroglycerin, to make dynamite, is an infusorial earth found near Hanover; but any non-plastic, porous, silicious substance may be employed, provided that it be sufficiently finely pulverised. The author made use of burnt clay from glass works. The dry powder was put into stoneware vessels and moistened with nitroglycerin in the proportion of 20—25 p. nitroglycerin to 80—75 p. powder. The mixture was well stirred with a wooden spatula.

Use.—Its use differs from that of nitroglycerin; for whilst a small charge of gunpowder will cause the latter to detonate, a large quantity of gunpowder or a charge of fulminate of mercury is required to produce the same result with dynamite. The nitroglycerin shows no tendency to separate from the silica. Dynamite will bear the shock of a hammer on an anvil without exploding.

The author describes the construction of the cartridges which he used, and gives ample details of comparative experiments made at Montreuil and Paris.

Conclusions.—Dynamite is not exploded by a blow or by contact with flame.

1. In the blasting of rocks, excavation of trenches, and generally in all cases where bursting effects are desired, dynamite is, in equal weights, much more powerful than gunpowder. The fractures extend to a great distance from the blast, and the saving of expense in removing the fragments amounts to 25—30 per cent.

2. The experiments made with shells show that the effects vary with the strength of the shell; the number of fragments produced varies directly as the quantity of dynamite employed, and is always much greater than would be produced by an equal volume of powder. It is necessary that the shells should be much thicker than usual, or the fragments, being so small, would not retain sufficient projectile force. It is thought that there will be no danger of the shell bursting in the gun, but experiments are desirable.

3. Dynamite may be advantageously used to render cannon unserviceable, instead of spiking them.

This is best effected by putting the charge of dynamite into the bore

* Moniteur Scientifique, xiii, 91—94.

of the gun and closing the mouth with a conical wooden plug; the dynamite may be fired by a Bickford fuse.

4. Dynamite would seem to be less suitable than blasting-powder for charging fougasses. It would seem to be especially suitable for use in submarine torpedoes.

5. Whenever gunpowder is applicable to the destruction of palissades, walls, bridges, piles, &c., it may, with marked advantage, be replaced by dynamite.

The author has also observed* that the paper envelope in which dynamite is made up into cartridges, absorbs nitro-glycerin, and in contact with a sufficient mass of porous material, will in time wholly remove the nitro-glycerin from the dynamite, and he thinks that this is a possible source of danger, &c.

F. H. H.

Note on the Use of Dynamite for Breaking up Large Castings, &c. By P. Champion.†

The experiments were made on a mass of metal weighing about 5000 kilograms, or about 5 tons, 1·20 m. long, 60 centimetres high, and 80 centimetres wide.

On one side three holes were bored 25 millimetres in diameter, 45 centimetres deep. The central hole received a charge of 150 grams of dynamite containing 75 per cent. nitroglycerin in two cartridges. The first weighing 120 was carefully rammed in; the second containing the match was introduced in contact with the first, the empty space being filled with sand. The first explosion divided the block into two parts; the two others broke up these into many large pieces. Two other mines 25 centimetres deep divided these pieces into fragments suitable for fusion.

The author in conclusion suggests that the use of electricity in order to render the several explosions simultaneous, would be attended with the best results; as by the use of matches, the explosion of one mine often disturbs the arrangement or the tamping of one close by. And besides, simultaneous explosions would at once break up a mass into fragments small enough for immediate use.

E. T. C.

* Compt. rend., lxxii, 688. † Ibid., 770.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXIII.—*On Tetrabromide of Carbon. No. II.*

By Thomas Bolas and Charles E. Groves.

In a former paper* we described several methods for the preparation of the hitherto unknown tetrabromide of carbon, and in the present communication we desire to lay before the Society the results of our more recent experiments. In addition to those methods of obtaining the carbon tetrabromide, which we have already published, the following are of interest, either from a theoretical point of view, or as affording advantageous means for the preparation of that substance.

Action of Bromine on Carbon Disulphide.

Our former statement that† bromine had no action on carbon disulphide requires some modification, as we find that when it is heated to 180° or 200° for several hundred hours with bromine free from both chlorine and iodine, and the contents of the tubes are neutralised and distilled in the usual way, a liquid is obtained, which consists almost entirely of unaltered carbon disulphide; but when this is allowed to evaporate spontaneously, a small quantity of a crystalline substance is left, which has the appearance and properties of carbon tetrabromide. The length of time required for this reaction, and the very small relative amount of substance obtained, would, however, render this quite inapplicable as a process for the preparation of the tetrabromide.

Action of Bromine on Carbon Disulphide in presence of Certain Bromides.

Having noticed in our former paper the remarkable influence which the presence of antimony terbromide had when added to the mixture of bromine and carbon disulphide, we thought it would be interesting to study the effect produced when other bromides were substituted for that of antimony, and for this purpose selected the bromides of the following elements:—bismuth, arsenic, gold, platinum, cadmium, zinc, nickel, iron, tin, phosphorus, and sulphur. These bromides may, for our purpose, be divided into two groups, the first of which, comprising the metals bismuth, arsenic, gold, platinum, cadmium, zinc, and nickel,

* Chem. Soc. J. xxiii, 161. † Ibid.

give results so far satisfactory that they might be substituted for the antimony bromide in the preparation of tetrabromide of carbon; but notwithstanding this we consider bromide of iodine in presence of excess of bromine to be the most convenient agent for converting carbon disulphide into carbon tetrabromide.

When heated with bisulphide of carbon and excess of bromine for a considerable time, bismuth converts a large proportion of the disulphide into tetrabromide, apparently yielding a result as good as that obtained with antimony; arsenic bromide under similar circumstances also transformed the greater portion of the carbon disulphide. These three elements, antimony, arsenic, and bismuth, as might have been expected from the great similarity in their chemical relations, yielded results which differed but little from one another.

Carbon disulphide was enclosed in a sealed tube along with one atomic proportion of metallic bismuth, and somewhat more than nine of bromine, and then heated for about sixty hours to a temperature of 180° to 190° C. The contents of the tube, when opened, had an odour of the carbon sulphobromide which is described in another part of this paper. After the addition of an excess of sodium hydrate, the product was submitted to distillation in the usual way, when carbon tetrabromide, together with a small quantity of unaltered carbon disulphide, was obtained. The experiment with arsenic bromide was conducted in a precisely similar manner, substituting metallic arsenic for the bismuth, the conversion of the disulphide into tetrabromide being even more complete than in the previous case. Gold when heated with the proper proportions of carbon disulphide and bromine in the manner above described, determined the formation of a considerable quantity of carbon tetrabromide. Platinum under similar circumstances also yielded a very satisfactory result. In the case of cadmium and zinc, it was necessary to add their bromides to the mixture of bisulphide of carbon and bromine, as we find that the metals themselves are scarcely acted upon by dry bromine, even at a temperature of 180°. Nickel was used in the metallic state. The last three experiments, namely, those with cadmium, zinc, and nickel, yielded results which are somewhat inferior as regards the quantity of tetrabromide formed. The last four elements in the above list, viz., iron, tin, phosphorus, and sulphur, when heated with carbon disulphide and bromine, gave unsatisfactory results, although in each case when the product was neutralised and distilled, after the water was separated and the excess of unaltered disulphide allowed to evaporate spontaneously, a white crystalline substance remained behind, which was identified as carbon tetrabromide, although the quantity obtained was insufficient for analysis.

Decomposition of Bromopicrin under the Influence of Heat.

Stenhouse has observed that when bromopicrin is heated to a temperature a little above 100°* it decomposes with explosive violence, and we also found† that when a test-tube containing a few drops of the substance was strongly heated, a slight explosion ensued. When, however, a considerable quantity was cautiously and gradually heated, it became of a dark brown colour, from liberation of bromine, and decomposed quietly. From this it might be inferred that the explosion observed by Stenhouse and ourselves arose from the exposure of the vapour to a high temperature. This is well known to be the case with ethylic nitrate, and various other compounds which contain the higher oxides of nitrogen. The probability of this is increased from the fact that, during an experiment in which some ounces of bromopicrin were being distilled under the ordinary atmospheric pressure, the greater portion of it passed over without accident; but when the level of the liquid in the retort had become very low, so that the sides were strongly heated, a violent explosion took place, which shattered the apparatus.

With the object of more accurately ascertaining the nature of the decomposition which bromopicrin undergoes when submitted to the influence of heat, we determined to study its effect on a considerable quantity of the substance. After some preliminary trials to ascertain the best method of attaining this end, an apparatus was arranged in the following manner:—One arm of a Y-tube condenser was connected with a small bolt-head by means of a digestion-tube bent twice at right angles, the longer limb of which had a length of about 60 centimetres. The other arm of the condenser communicated with the atmosphere through a two-necked Woulfe's bottle containing a layer of concentrated sulphuric acid, to intercept moisture; the tubes passed down to within a short distance of the acid, but did not dip into it. The condenser was kept cool by surrounding it with water contained in an inverted bell-jar, the tubulure passing through the neck and being connected there with the receiver. All the joints were fitted by means of caoutchouc corks.

It was found convenient to employ in each operation from 200 to 300 grams of bromopicrin, which were introduced into the bolt-head, and cautiously heated, when the liquid gradually became of a dark brown colour, from liberation of bromine, and after a time a brisk reaction set in. As soon as this took place, the light was removed, and the decomposition allowed to proceed without the aid of external heat: a considerable quantity of a dark red volatile liquid collected in the

* Ann. Chem. Pharm., xci, 309. † Jour. Chem. Soc., xxiii, 154.

receiver, whilst nitrogen oxides and carbonic anhydride escaped by the exit-tube. After the first violence of the reaction was over, a gentle heat was applied, and the digestion continued for 30 or 40 hours, taking care that the bromopicrin did not distil over. In order to ascertain the progress of the decomposition, the contents of the bolt-head were tested from time to time by mixing a sample with water, and when this became solid, the digestion was discontinued. The dark-red liquid in the bolt-head, which, when allowed to stand some time, generally deposited very large tabular crystals of tetrabromide of carbon, was now mixed with water, and sufficient sodium hydrate added to neutralise the bromine. On heating the solution, the carbon tetrabromide fused into a cake under the liquid, but unless the digestion had been continued for a somewhat longer time than that above mentioned, it generally contained traces of bromopicrin; this, however, could be easily removed by heating it with an aqueous solution of potassium cyanide, which is without action on the tetrabromide of carbon, but entirely destroys the bromopicrin.*

The tetrabromide of carbon thus obtained was found to contain a minute quantity of an oily substance, which was removed by powerful pressure between folds of bibulous paper before crystallisation. Analyses of the pure substance were then made with the following results:—

VII. 616 grm. substance gave 1·393 grm. silver bromide.
VIII. 4625 grm. substance gave 1·0435 grm. silver bromide.
IX. 185 grm. substance gave ·419 grm. silver bromide.

		Theory.	VII.	VIII.	IX.	Mean.
C ..	12	3·61	—	—	—	—
Br_4..	320	96·39	96·23	96·01	96·36	96·20
	332	100·00				

VII and VIII were made in the usual way by burning with pure lime. IX was made by introducing a weighed quantity of the substance into a tube, together with a sufficient quantity of a solution of sodium ethylate in alcohol, sealing the tube, and heating it to 100° C. for five or six hours. At the expiration of that time, it was carefully opened, and the contents diluted with a considerable quantity of water. The analysis was then proceeded with in the usual way.

The dark-red liquid which had collected in the receiver during the decomposition of the bromopicrin above described, was next examined

* When bromopicrin is heated with an aqueous solution of potassium cyanide, it is entirely decomposed, cyanogen bromide being at first formed; but on further application of heat, this is destroyed, whilst a compound of a dark brown colour remains in solution.

by submitting it to fractional distillation. The flask in which the liquid was heated, was connected with a digestion-tube about two metres in length, having a tubulure fused in near the top, at right angles to the main tube, the bulb of the thermometer, which was inserted in the top of the main tube, being just below the junction with the tubulure. The latter was connected with a condenser arranged in a manner similar to that employed in the decomposition of bromopicrin. In order to expel, as far as possible, any gaseous products that might have been dissolved in the liquid under examination, it was at first heated to such an extent, that the vapour which condensed in the main tube and ran back into the distilling flask, reached to within a few centimetres of the thermometer-bulb. As soon as most of the dissolved gas had been thus expelled, the heat was increased, so that the vapour might pass over into the condenser. The column of mercury in the thermometer then rose rapidly, until it reached 56°, at which temperature the bulk of the liquid distilled over. It is almost unnecessary to state that the apparatus was sheltered as much as possible from draughts during the operation. The portion which came over between 56°—56·5° C. was submitted to analysis.

I. 247 grm. substance gave ·600 grm. silver bromide.
II. 414 grm. substance gave ·900 grm. silver bromide.

I corresponds to 93·18 per cent. bromine, and II to 92·51 per cent. bromine, mean 92·84 per cent. This liquid had the dark brown colour and general appearance of bromine, but differed from it in having a somewhat lower boiling point, namely, 56·5°, whereas bromine boils at 59·5.°* It is moreover readily soluble in water, yielding a pale-yellow solution, which was found to contain hydrobromic acid, nitric acid, and free bromine. When a small quantity of water is added to the liquid, it evolves much gas. With concentrated sulphuric acid it forms a colourless crystalline compound. It is very pungent, and attacks the eyes strongly, like chloropicrin. It destroys caoutchouc far more rapidly than bromine, causing it to swell up and become brittle. The analysis of this liquid does not enable us to decide whether it is simply a solution of a nitrogen oxide in bromine, or a definite compound containing nitrogen, oxygen, and bromine. Considering, however, its remarkably constant boiling point and general properties, we are inclined to believe the latter. The compound $NOBr_4$ requires 91·42 per cent. bromine, and the substance under consideration contains 92·84 per cent.

* As the boiling point of bromine given in the Handbooks varies so much (45° to 63°), we thought it would be expedient to make a tolerably accurate determination, and found that when a considerable quantity of dry bromine was distilled under a pressure of 751 mm., it passed over between 59·5° and 59·75°, the stem of the thermometer being in the vapour.

From the results of these experiments on the decomposition of bromopicrin, it might appear probable that the tetrabromide of carbon obtained by processes (*c*) and (*d*)* (antimony terbromide, or iodine bromide, with excess of bromine on bromopicrin) resulted, not from any particular action exerted by the antimony bromide or bromide of iodine, but simply from the splitting up of the bromopicrin under the influence of heat. This, however, is not the case, as in experiments (*c*) and (*d*) the flask containing the materials was heated in a water-bath, and we have ascertained that bromopicrin alone does not decompose at 100° C. The action of heat on bromopicrin just described affords a ready and expeditious method of preparing small quantities of carbon tetrabromide, the yield being about 30 per cent.

Action of Bromine on Iodoform.

The action of bromine on iodoform at the ordinary temperature has been studied by Serullas,† and subsequently by Bouchardat,‡ who found that a portion of the iodine in the iodoform was replaced by bromine, forming bromiodoform, CBr_2IH. From a consideration of the results of their experiments, it seemed likely that an excess of bromine, acting upon iodoform at a high temperature, would convert it into tetrabromide of carbon. In order to test the correctness of this supposition, one part of iodoform was introduced into a tube, and six times its weight of bromine added to it, when the mixture became warm, and much iodine was liberated. The tube was then sealed and heated to about 180° for 70 hours, and on opening it at the expiration of that time, a considerable quantity of hydrobromic acid escaped. The contents were then neutralised with sodium hydrate, and distilled in the usual way. The semi-solid crystalline mass, after being separated from the water, and having the greater portion of the oily matter removed by pressure, was examined, and found to be carbon tetrabromide, contaminated with a minute quantity of the above mentioned oil, which was, however, easily removed by crystallisation from spirit. In this experiment bromiodoform was undoubtedly first produced, the liberated iodine combining with the excess of bromine, and the bromide of iodine thus formed acting upon the bromiodoform, transformed it into tetrabromide of carbon.

Action of Bromide of Iodine and Bromine on Chloroform.

As the last atom of hydrogen in bromoform had been so easily replaced by the action of bromide of iodine and excess of bromine,

* Chem. Soc. J. xxiii, 162.

† Ann. Ch. Phys. [2], xxxiv, 225, and xxxix, 97.

‡ J. Pharm., xxiii, 10.

forming tetrabromide of carbon,* we thought that if chloroform were submitted to the same treatment, the last atom of hydrogen in it might likewise be replaced by bromine, forming bromochloroform (trichlorbromomethane) $CBrCl_3$. Dry chloroform was, therefore, heated to 150° with one part of iodine and three of bromine for three hours, when the tubes were opened to allow of the escape of the gas produced during the reaction; the tubes were then again closed and the heating continued until they ceased to emit gas when opened. The contents were then neutralised and distilled in the usual way, when a colourless liquid, having an ethereal odour, was obtained, which was submitted to fractional distillation. It began to boil at 95°, the temperature gradually rising, until at 200° the greater portion had passed over. From the temperature at which this mixture began to boil, it was evident that all the chloroform had been converted into other products. The lowest fraction (100° to 130° C.) was liquid at ordinary temperatures; the intermediate ones deposited large colourless crystals when cooled, and the highest (180° to 200° C.) at once solidified to a crystalline mass, somewhat resembling tetrabromide of carbon, which when crystallised from spirit, melted at 69°; another recrystallisation raised it to 70°. An analysis of this portion yielded the following results:—

·199 grm. substance gave ·466 grm. mixed silver bromide and chloride, containing ·286 grm. metallic silver; this is equivalent to ·1545 grm. bromine and ·0255 grm. chlorine. This corresponds to 77·62 per cent. bromine and 12·81 of chlorine. The compound CBr_3Cl requires 83·48 bromine and 12·35 chlorine.

Another rectification of the higher fraction yielded a substance which, after crystallisation from spirit, melted at 76° C., and on analysis gave 92·91 per cent. bromine and 3 per cent. chlorine. Tetrabromide of carbon containing 96·39 per cent. bromine, it would seem that the substance is simply the tetrabromide contaminated with a small quantity of CBr_3Cl. From the analyses it would appear that tetrabromide of carbon, CBr_4, and tribromochloromethane, CBr_3Cl, are amongst the products obtained, and this unexpected result induces us to believe that the hydrogen in the chloroform is removed as hydrochloric acid; but the reaction requires further investigation.

In preparing tetrabromide of carbon from disulphide of carbon, it is necessary to employ a considerable excess of soda in order to decompose a sulphur-compound (sulphobromide of carbon), which otherwise comes over with the vapour of water, thus contaminating the tetrabromide of carbon. We have observed that there is always a small quantity of an oily substance present, together with the tetrabromide prepared by this process; it is advisable to remove this substance by

* Chem. Soc. J., xxiii, 163.

pressure before it is finally purified by distillation, or crystallisation from spirit.

Boiling point and Specific Gravity of Carbon Tetrabromide.

We thought it would be of interest to ascertain the boiling point of tetrabromide of carbon both at the ordinary and at diminished pressures; and two parallel series of experiments were therefore made with the tetrabromide prepared from bisulphide of carbon and from bromopicrin. The following table gives the results. Column I represents the pressure in millimetres; column II the boiling-point of the tetrabromide derived from carbon disulphide; column III the boiling point of that from bromopicrin:—

I. mm.	II. CBr_4 from CS_2.	III. CBr_4 from CNO_2Br_3.
50	101·75	101.75
100	120·50	121·00
228	143·00	143·50
280	150·00	150·50
380	160·25	161·00
430	—	165·50
482	—	169·50
558	—	175·00

Tetrabromide of carbon under the ordinary pressure (760 mm.) boils at 189·5°, but at the same time it undergoes a slight decomposition, bromine being liberated. It can, however, be distilled without change *in vacuo*, but, when the pressure is increased to about 350 mm., a very slight decomposition commences. For this reason the experiments on the distillation of the tetrabromide from carbon disulphide, under diminished pressure, were not carried on above 380 mm., as the results corresponded so nearly with those in column III.

Several determinations were made of the specific gravity of tetrabromide of carbon obtained both from carbon disulphide and from bromopicrin; but owing to the fused substance crystallising as it cooled and forming cavities, the results were not so concordant as we could have wished. The highest result, however, and that which is probably the most correct, gave 3·42 as the specific gravity of carbon tetrabromide at a temperature of 14° C. When heated to 200° in a sealed tube, it undergoes partial decomposition, a small quantity of bromine being liberated. The same phenomenon takes place when the tetrabromide is exposed to bright sunshine, the substance at the same time showing a strong tendency to crystallise on the side of the tube nearest the light, in well-formed and very brilliant crystals.

Sulphobromide of Carbon.

During the preparation of tetrabromide of carbon by the action of bromine and bromide of iodine on bisulphide of carbon, we did not observe that substance immediately on neutralising, and it seemed probable that some intermediate product was formed which was afterwards decomposed by excess of sodium hydrate, yielding the tetrabromide. In order to satisfy ourselves that this was really the case, some bisulphide was heated with bromine and iodine in the way already described, and the product was poured into water. The iodine and excess of bromine were then removed by the cautious addition of dilute soda-solution, taking care that the liquid never became alkaline, which was easily accomplished, as bromine is somewhat soluble in a solution of sodium bromide. The slightly-coloured heavy oil was then separated from the aqueous liquid, dried by calcium chloride, and submitted to fractional distillation. In the first place a small quantity of unaltered carbon disulphide distilled over, and the liquid assumed a much darker colour, from incipient decomposition; the temperature then rose rapidly, and the bulk of the liquid came over between 150° and 165°. There was, however, considerable decomposition. A determination of the sulphur in the portion boiling at 165° was made, and found to be 7·81 per cent. The formula CBr_2S requires 15·69 per cent. From this it would appear that the liquid obtained was very far from being pure carbon sulphobromide, but is that compound contaminated with carbon tetrabromide. Its odour somewhat resembles that of carbon sulphochloride, and, when heated with excess of soda-solution, it yields at once pure tetrabromide of carbon. Careful rectification *in vacuo* would probably yield more satisfactory results.

When bisulphide of carbon was heated with bromide of iodine and water, together with a large excess of bromine to 100°, it was completely decomposed, and, on opening the tube, a large quantity of gas was evolved, but no tetrabromide could be detected after the contents had been neutralised. The gas, which was principally hydrobromic acid, had an odour resembling that of phosgene, although not so well marked as that pointed out in our former paper, when carbon tetrabromide is heated with sulphuric acid. It is highly probable that this is due to carbonyl dibromide (bromophosgene) $COBr_2$, which could doubtless be obtained by heating carbon tetrabromide and sulphuric anhydride in a manner precisely similar to that in which Schützenberger* obtained carbonyl dichloride (phosgene) from carbon tetrachloride.

* Compt. rend., lxix, 352.

Carbon Tetrabromide and Silver Oxalate.

In order to study the action of carbon tetrabromide on silver oxalate, a preliminary experiment was made by heating a small quantity of silver oxalate with excess of the tetrabromide. A reaction took place, accompanied by evolution of gas and production of a substance having a peculiar pungent odour. It was therefore thought advisable to repeat the experiment on a larger scale with weighed quantities of material. Four grams of silver oxalate and two grams of carbon tetrabromide were placed in a stout glass tube previously closed at one end; the other end was then drawn out and bent over, so that any gas evolved might be collected over mercury. The tube was heated in a water-bath; but when the temperature had nearly reached 100° a violent explosion took place, shattering the cast-iron vessel employed as a water-bath and distorting the tripod on which it was placed. Owing to this unexpected result, we have not as yet repeated the experiment.

Action of Ammonias on Carbon Tetrabromide.

Hofmann* has shown that the action of aniline upon the tetrachlorinated derivative of marsh-gas, CCl_4, yields triphenylated carbotriamine, or triphenylguanidine, $N_3\left\{\begin{matrix} C'''' \\ (C_6H_5)_3, \\ H_2 \end{matrix}\right.$ and although he did not succeed in preparing the carbotriamine itself from carbon tetrachloride when ammonia was substituted for aniline, he subsequently found that it could be obtained from chloropicrin.†

Action of Aniline on Carbon Tetrabromide.

Aniline acts with far greater readiness on the tetrabromide than on the tetrachloride of carbon. When one part of carbon tetrabromide was added to two parts of aniline and gently warmed, it dissolved, and on increasing the temperature to the boiling point, the mixture acquired an intense red colour. In a few seconds a powerful reaction set it, which completed itself without any further application of heat, and on cooling, the mixture solidified to a mass of crystalline plates.

$$6\left.\begin{matrix} C_6H_5 \\ H_2 \end{matrix}\right\}N + CBr_4 = \left.\begin{matrix} C'''' \\ (C_6H_5)_3 \\ H_3 \end{matrix}\right\}N_3.Br + 3\left[\left.\begin{matrix} C_6H_5 \\ H_3 \end{matrix}\right\}N.Br.\right]$$

When boiled with water, it almost entirely dissolved, and the solu-

* Proc. Roy. Soc., ix, 284. † Ann. Chem. Pharm., cxxxix, 107.

tion treated with excess of caustic alkali set free the mixed bases. On being distilled with water, the aniline passed over with the aqueous vapour, whilst the triphenylguanidine remained in the retort. The base was converted into the hydrochlorate, purified by crystallisation, and a platinum salt prepared from it, which, when submitted to analysis, gave the following result:—

·244 grm. platinum salt gave ·048 grm. platinum. This corresponds to 19·67 per cent. platinum, the theoretical for $2\left[\left.\begin{matrix} C'''' \\ (C_6H_5)_3 \\ H_3 \end{matrix}\right\}Br,\right]$ $PtCl_4$, being 20·04 per cent.

Action of Ammonia on Carbon Tetrabromide.

As the action of carbon tetrabromide on aniline is much sharper than that of the tetrachloride, taking place as it does so much more readily, and at the same time yielding a product which is almost entirely free from the black tarry substance which accompanies the triphenylguanidine obtained from the tetrachloride, we thought it probable that more favourable results would be obtained by the action of ammonia on tetrabromide of carbon than those obtained by Hofmann with the tetrachloride.* We therefore heated to 100° in a sealed tube for twelve hours, two parts of tetrabromide of carbon with one of ammonia dissolved in about sixteen of alcohol. At the expiration of that time, the solution had acquired a deep yellow colour, and on distilling it, the addition of water to the first portions of the distillate caused the separation of an oily substance heavier than water. This oil had the odour and taste of bromoform, and distilled between 144° and 146°. According to Borodine,† bromoform boils at about 145°. When submitted to analysis it gave the following results:—

I. ·398 grm. substance gave ·887 grm. silver bromide.

		Theory.	I.
C	= 12	4·74	—
Br_3	= 240	94·86	94·84
H	= 1	·40	—
	253	100·00	

It would appear therefore that bromoform is one of the principal products in this experiment, the quantity obtained being about one-half that of the tetrabromide of carbon originally employed. The solution from which the bromoform had been removed by distillation contained a considerable quantity of ammonium bromide, and was treated successively with silver sulphate, barium hydrate, and hydro-

* Ann. Chem. Pharm., cxxxix, 110. † Kekulé, Lehrb. ii, 145.

chloric acid, to convert the bromides into chlorides. After separating the ammonium chloride, platinum tetrachloride was added to the solution, when a small quantity of guanidine platino-chloride was obtained.

Action of Alcohol on Carbon Tetrabromide.

It naturally suggested itself that the bromoform obtained in the reaction just described, was formed by the mutual action of the alcohol and tetrabromide, independently of the ammonia; and with the object of ascertaining the correctness of this hypothesis, a solution of carbon tetrabromide in alcohol was heated to 100° for twelve hours. On opening the tube, a strong odour of aldehyde was apparent, and when the contents were distilled and water added to the first portions which came over, bromoform was precipitated. The amount of bromoform obtained in this operation was about three-fourths of the carbon tetrabromide originally employed, but on rectification it was found to contain a small percentage of unaltered tetrabromide. The formation of aldehyde and hydrobromic acid which we had previously noticed* shows that the decomposition takes place in the following manner:—

$$CBr_4 + C_2H_6O = CHBr_3 + HBr + C_2H_4O.$$

The quantity of bromoform obtained corresponds to this equation, theory requiring 76·2 per cent., while experiment gave 75·0 per cent. The principal action of alcoholic ammonia on carbon tetrabromide is undoubtedly similar to that of pure alcohol, which accounts for the small quantity of guanidine we obtained.

Action of Antimony on Carbon Tetrabromide.

When these two substances were heated together, the tetrabromide lost a portion of its bromine, and on continuing the heat a carbonaceous substance was produced. The results did not encourage further investigation.

Recovery of Bromine from Residues.

As a large quantity of bromine was obtained in this research in the form of residues, it was a matter of some importance to us to find a more convenient process of recovering the bromine than distillation with sulphuric acid and peroxide of manganese. After several trials we found the following to be the best method. The solution of the alkaline bromide is introduced into a retort with the requisite quantity of acid potassium chromate in crystals, and an excess of sulphuric acid previously diluted with half its weight of water is gradually added

* Journ. Chem. Soc., xxiii, 164.

through a thistle-funnel. After the first powerful reaction is over, heat may be applied to the retort. By employing the acid chromate, almost the whole of the bromine is readily recovered, and there is no danger of breaking the retort. We may also allude to the great advantage we have derived when working with bromine, from the use of the charcoal respirator invented by Dr. Stenhouse, as with it and a suitable mask for the eyes, the operator may work with ease in an atmosphere highly charged with bromine-vapour.

XXIV.—*On the Action of Normal and Acid Salts upon Ammonium Salts, especially upon Ammonic Chloride.*

By Reginald C. Woodcock, Student at the Royal College of Chemistry.

H. Rose* investigated in 1847 the action of sal-ammoniac at a high temperature upon different metallic oxides and salts, and found that, for the most part, chlorides of the respective metals were formed, some of which, *e.g.*, the chlorides of ammonium, iron, &c., were readily volatilised. Rose observed also that basic oxides of the formula $M''O$, such as CoO, NiO, MnO, FeO, likewise oxides of the formulæ $M_2''O$, such as Cu_2O, decompose ammonic chloride, when heated in an aqueous solution, with evolution of ammonia gas and formation of fixed metallic chlorides, whereas not one of the sesquioxides has this power.

These reactions are of great use in qualitative and quantitative analysis. Rose found that borax is not changed when ignited with ammonic chloride, that sodic phosphate is converted into sodic chloride and a little phosphorous chloride, whilst calcic phosphate is not affected, and that alkaline chromates leave chromic oxide and alkaline chlorides; but he appears to have omitted to study the changes which are produced when various salts are heated in aqueous solution with ammonium salts, more especially with the chloride.

Bolley† observed in 1848 that free ammonia is evolved on mixing solutions of borax and ammonic chloride in the proportions of one molecule of the former to one of the latter; the solution when slowly evaporated, deposited crystals requiring five or six parts of water for their solution, and exhibiting the composition $B_8O_{11}Na_{02} + 10H_2O$. The solution of this salt had no action, either upon litmus or upon turmeric paper, and on the addition of *dilute* sulphuric or nitric acid, gave a white precipitate of boric acid. Bolley found that an excess

* Pogg. Ann., lxxiii, 582. † Ann. Ch. Pharm., lxviii, 122.

of ammonic chloride converts the borax entirely into common salt and boric acid; he based upon this observation some interesting speculations regarding the presence of boric acid in fumaroles, and suggested that native boric acid may probably have been produced by the action of ammonic chloride upon minerals containing this acid.

I have observed that various other salts containing fixed bases when brought together, in the dry state, or in aqueous solution, with ammonic chloride, likewise decompose the latter, with formation of fixed metallic chlorides and evolution of gaseous ammonia, and have thought it of sufficient interest to determine quantitatively the amount of ammonia so evolved. This was done by heating in a retort weighed quantities of sal-ammoniac and salts to be operated upon, and collecting the ammonia by passing it through a solution of semi-normal sulphuric acid. I found that various other salts, besides borax, evolve ammonia most readily, but that the decomposition is more or less sluggish, according to the nature of the salts employed, the reaction being based upon the formation of acid salts from various normal saline compounds, part of the base being removed as chloride, thus giving rise to the evolution of ammonia. I examined, among other salts, the action of sal-ammoniac upon normal potassic chromate, phosphates, microcosmic salt, or hydro-ammonic sodic phosphate (this latter, being prepared by mixing the common sodic phosphate with ammonic chloride, is known to evolve ammonia when heated in aqueous solutions) upon trisodic and common or hydro-disodic phosphate, upon dipotassic tartrate, dipotassic succinate, trisodic citrate, &c., &c., and I have determined *quantitatively* the amount of ammonia evolved from aqueous solutions of the sodic metaborate and common borax, as well as from normal potassic chromate and acid sodic phosphate.

On mixing weighed quantities of carefully prepared sodic metaborate (obtained by igniting borax with sodic nitrate till the whole of the nitrate was decomposed) with weighed quantities of sal-ammoniac in the proportion of four molecules of sodic metaborate to two of ammonic chloride, ammonia was evolved most copiously, and the whole decomposed very rapidly and completely, leaving only the biborate and sodic chloride, according to the equation—

$$4BONao + 2AmCl = B_4O_5Nao_2 + 2NaCl + 2NH_3 + OH_2.$$

2·466 grms. of sodic metaborate, mixed with 1 grm. of ammonic chloride, and dissolved in about 2 ounces of water, evolved, when submitted to distillation, ammonia equal to 99·51 per cent. of the ammonic chloride employed.

3·57 grms. of commercial borax mixed with ·500 grm. of ammonic chloride, and dissolved in about 2 ounces of water, gave on distil-

lation, 100·04 per cent. of the ammonic chloride employed. The decomposition may be expressed by the equation—

$$2B_4O_5Nao_2 + 2AmCl = B_8O_{11}Nao_2 + 2NaCl + 2NH_3 + OH_2.$$

This sodic tetra-metaborate is the salt prepared and described by Bolley.

I studied these reactions again, because the changes produced by normal potassic chromate upon ammonic salts, which I was then examining, were not so sharp and concise as might have been expected, and also in the hope of providing a substitute for the slaked lime or caustic soda usually employed for liberating ammonia from various ammoniacal salts, the temperature at which the gas comes off being so much less.

Normal and acid borates may be employed with advantage for setting free ammonia from its salts, and the reaction is both neat and perfect, no frothing taking place. The expectation of being able to evolve ammonia from ammonic salts in presence of nitrogenous bodies, such as urea, without the latter undergoing partial decomposition, was not realized, for on boiling a solution of urea (2 molecules) with sodic metaborate (4 molecules), 10·88 per cent. of ammonia were evolved, the total possible amount being 56·66 per cent.

Tri-sodic, as well as hydro-disodic phosphate, readily decompose ammonic salts:—

3·551 grms. of crystallised trisodic phosphate, when mixed with ·5 grm. of ammonic chloride and distilled from an aqueous solution, gave off ammonia gas equal to 100·04 per cent. of the ammonic chloride employed. 3·345 grms. of common sodic phosphate distilled from an aqueous solution with ·5 grm. of ammonic chloride, yielded ammonia corresponding only to 75·69 per cent. of ammonic chloride employed.

This latter experiment, when viewed in connection with the known fact that a solution of microscosmic salt is capable of yielding ammonia when boiled in aqueous solutions, probably giving rise to the formation of dihydro-sodic phosphate, appears to show that the tendency to form acid salts, which in the borates is so pronounced, as to yield (according to Bolley) boric acid, by the continuous action of sal-ammoniac upon a solution of borax, does not hold good in the case of phosphates.

Normal alkaline, as well as other soluble and insoluble metallic chromates, evolve ammonia when distilled in aqueous solution with ammonic salts. This reaction attracted my attention, more especially; metallic chlorides are formed, and an acid chromate or bichromate is left, according to the equation:—

$$2CrO_2Ko_2 + 2AmCl = Cr_2O_5Ko_2 + 2NH_3 + 2KCl + OH_2.$$

On dissolving equivalent quantities of the two salts, submitting the mixture to long continued ebullition, and absorbing the evolved ammonia gas in a standard solution of sulphuric acid, I was never able to obtain the theoretical amount of ammonia corresponding to the quantity of ammonic chloride employed.

1·859 grm. of pure dipotassic chromate were mixed in an aqueous solution with 0·5 grm. of ammonic chloride, and boiled in a retort during several hours, as long as any ammonia was evolved. The yield of ammonia corresponded to 81·6 per cent. of the ammonic chloride employed.

Digestion in sealed tubes had no better effect:—

1·817 grm. of dipotassic chromate digested in a sealed glass tube at 100° C., yielded on distillation ammonia equal to 84·53 per cent. of the ammonic chloride employed.

Slight excess of one or the other salt did not appear to affect the reaction in any marked manner.

2 grms., *i.e.*, excess of dipotassic chromate, digested with ·5 grm. of ammonic chloride in a sealed tube for about an hour at 100° C., yielded on distillation ammonia corresponding to 81·32 per cent. of ammonic chloride.

1·859 grm. of dipotassic chromate, when heated in a sealed tube with ·7 grm. (or excess) of ammonic chloride, yielded ammonia corresponding to 81·6 per cent. of ammonic chloride.

I was able to trace the reaction somewhat more fully by distilling on a larger scale theoretical quantities of the two salts. I employed 65 grms. of dipotassic chromate and 17·87 grms. of ammonic chloride, distilled as long as any ammonia came off, and collected the gas so evolved in dilute hydrochloric acid, from which the crystalline salt was obtained by evaporation. The contents of the retort were then turned out into an evaporating dish, and the solution concentrated till dipotassic dichromate crystallised out. The crop of crystals so obtained was recrystallised, and then submitted to analysis. The salt gave in two experiments 36·05 and 36·10 per cent. of chromium. The theoretical percentage of chromium in bichromate being 35·59.

On evaporating the mother-liquor further down, ammonia gas was *again evolved most copiously*, and a further impure crop of crystals of dipotassic dichromate obtained. The mother-liquor contained the potassic chloride, a quantity of which I purified by crystallisation, and by removing the last traces of chromate by means of baric chloride.

It is evident, therefore, that the presence of a large excess of dipotassic dichromate prevents the complete decomposition of the ammonic chloride.

The action appears to be purely molecular, for on nearly neutralising some dipotassic dichromate with ammonia, and boiling the solution,

ammonia gas was evolved in abundance; but on the addition of a large excess of a solution of dichromate and again boiling, only the merest trace of ammonia was perceptible. It appears to be probable that ammonio-potassic chromate can exist in the presence of much acid chromate, and that, on the removal of a portion of dichromate, the normal ammonio-potassic chromate breaks up according to the equation:—

$$2CrO_2AmoKo = \left\{\begin{array}{l} CrO_2Ko \\ O \\ CrO_2Ko \end{array}\right. + 2NH_3 + OH_2.$$

Dr. Frankland has used for some time past excess of phosphoric acid, in order to prevent the loss of ammonia when evaporating polluted waters, sewage-waters, &c., before submitting the residues so obtained to organic analysis. Phosphoric acid was found to prevent the loss in proportion to the quantity of free acid present. May not this be explained from the analogous action of the acid chromate just described, by the formation of acid phosphates which fix ammonia and prevent the decomposition of ammonic salts?

I have only been able to make one experiment, which, however, tends to show the correctness of this view: for on distilling an aqueous solution of 3·551 grms. of trisodic phosphate (which, as we have seen, evolves the whole of the ammonia from the ammonium salt), together with ·5 grm. of ammonic chloride, and adding excess of the dihydrio-sodic phosphate (3 grms.), 23·5 per cent. of the ammonic chloride was decomposed.

The experiments I made with ammonic sulphate in place of ammonic chloride, had to be rejected, as it was found that the neutral sulphate evolves ammonia when boiled by itself in an aqueous solution, probably owing to the formation of an acid sulphate.

It deserves to be mentioned that this action upon ammonic chloride is not confined to normal alkaline chromates, but that insoluble chromates, such as baric or plumbic chromate, likewise evolve ammonia when boiled with ammonic chloride, with formation of acid chromates, and that ignited plumbic chromate appears to evolve ammonia more copiously than precipitated chromate.

In conclusion I would mention that ammonia is given off when normal sodic succinate is heated in an aqueous solution with ammonic chloride. The reaction may be expressed by the equation:—

$$S\bar{u}Nao_2 + AmCl = S\bar{u}HoNao + NaCl + NH_3.$$

The same holds good for normal potassic tartrate and normal citrate.

I am much indebted to Mr. Valentin for the assistance and advice he gave me whilst conducting these experiments.

XXV.—*Burnt Iron and Burnt Steel.*

By W. Mattieu Williams.

[Abstract of Paper read April 6, 1871.]

Iron which has been damaged by reheating is designated "burnt iron," by the workman, who also gives the same name to iron which has been excessively heated and exposed in the puddling furnace *after balling*. No amount of heat applied to iron in the blast-furnace or in the early stages of puddling produces burnt iron.

Burnt iron is brittle, its fracture is short, it displays the so-called "crystalline" structure, and it has lost the fibrous structure and silky fracture of good iron.

When steel has been raised to a yellow or white heat, and then suddenly cooled, it becomes brittle, and no longer capable of tempering, is worthless for the ordinary uses of steel until again raised to a welding heat, rolled or hammered, and allowed to cool gradually. Burnt steel has a coarse granular fracture, the facets of the granules being, for the most part, either rounded or conchoïdal. The conchoïdal facets serve practically as a distinguishing characteristic.

I have examined many samples of burnt iron, and find in all of them small particles of black oxide, more or less abundantly diffused throughout the mass of iron, suspended or entangled within it. I find no such particles of oxide in burnt steel, nor any other indication of internal oxidation of iron.

Important practical decisions often depend upon the determination of whether certain defects of particular samples of iron are due to burning or to other causes. I have devised a very simple means of answering this question. I take about a decigram of fresh borings or coarse filings, put them into a dry narrow test-tube, then pour upon them about three cubic centimetres of nitric acid diluted to sp. gr. 1·20. If the iron is burnt, the particles of dark oxide become separated from the metallic iron as it dissolves, and are suspended in the liquid, rendering it dark and turbid. They ultimately disappear and are thus distinguishable from particles of carbon, &c. This action is easily recognized by treating equal quantities of borings of burnt and of good iron simultaneously in the same manner, and comparing.

I find that ordinary sound wrought iron contains a small quantity of carbon, the most important function of which appears to be to prevent burning by its reducing agency As soon as the carbon is removed, oxidation commences when the iron is heated, and this oxidation is not merely superficial, but extends throughout the mass. The higher the temperature and the greater the amount of exposure to the atmosphere while heated, the greater is the quantity of carbon required for protecting the iron. This is, I believe, the reason why all attempts to make merchantable iron by the Bessemer process have failed. The high temperature, and the violent exposure of melted metal to the air forced through it, causes oxidation of the iron to commence even in the presence of much carbon. This oxidation or burning of the iron commences in the Bessemer converter, when the proportion of carbon is brought down to about 0·25 per cent. 0·20 per cent. may be stated as the practical minimum to which it is possible to bring down the carbon of Bessemer metal without destroying malleability, but this is rarely reached. About 0·28 is the lowest ordinarily aimed at by the manufacturer.

I find that iron attains its maximum toughness, when it is otherwise pure, and its carbon is reduced to the lowest possible proportion without oxidation of the iron commencing. Thus the success of the maker of armour-plates, ship-bolts, &c., depends upon his skill in exactly touching, without passing, the point at which the oxidation of carbon ceases, and that of the iron is about to begin. By skilfully conducting his last reheating processes by means of a reducing flame, he is able to work down to the lowest possible trace of combined protecting carbon, and thus obtain the maximum of toughness and extensibility.

I find, as the result of a large number of varied experiments, that whenever steel is raised to any temperature above the lowest visible red heat, and more or less exposed to the action of atmospheric air, its carbon is oxidised with a rapidity proportionate to the temperature and degree of exposure. These experiments have extended, through a series of various conditions, from low-heat and closed annealing furnaces to the great heat and excessive exposure of the Bessemer converter. This oxidation occurs not only at the surface, but proceeds inwards. It is now well known that certain gases can pass readily through heated iron, and thus the permeation of the oxygen and exclusion of the carbonic oxide no longer presents a difficulty. I, therefore, explain the structure and properties of "burnt steel" as the result of suddenly solidifying it from the viscous condition which it attains at a welding heat, and thereby imprisoning the carbonic oxide evolved by the oxidation of the carbon. By slower cooling the carbonic oxide would have become either occluded or expelled. This explanation accords with the fact that burnt steel may be cured, as above stated, by welding up the

cavities, or "toad's eyes," as the workmen call them, which are visible on the fracture of such steel. These, according to my explanation, are the minute bubbles formed by the carbonic oxide suddenly arrested in various stages of evolution or collapse.

According to the above, the workmen's term "burnt" is not incorrectly applied in either case, the rottenness of both the iron and the steel being caused by the presence of intermingled particles of combustion-products breaking the continuity of the metal. The carbon is burnt in the case of the "burnt steel," the iron itself in the "burnt iron."

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

Heat of Combustion of Magnesium, Indium, Cadmium, and Zinc. By A. Ditte.*

The author, continuing his investigations, shows that zinc oxide, when prepared in different ways, gives different results, and thus accounts for the discrepancy between Favre's figures and his own. Zinc oxide prepared by keeping the hydrate heated continuously for four hours to 350°, was perfectly white, and dissolved in dilute sulphuric acid with ease. The heat disengaged in the calorimeter was:—

	I.	II.	Mean.
For a gram	246·2	242·1	244·2
For an equivalent ..	10,096	9,928	10,012

When zinc hydrate was raised for a short time to a dull-red heat, an oxide was produced which required some time to dissolve in dilute sulphuric acid, and gave in the calorimeter the following results:—

	I.	II.	Mean.
For a gram	272·6	271·4	272·0
For an equivalent ..	11,182	11,127	11,155

When prepared by maintaining the nitrate or hydrate at a white heat for an hour, the oxide was light yellow, and dissolved with difficulty in the dilute acid. The results were as follow:—

	I.	II.	Mean.
For a gram	298·7	300·7	299·7
For an equivalent ..	12,247	12,339	12,288

In operating on indium the author found more difficulty. The metal is not attacked by the dilute acid until touched with a platinum-rod, and then very slowly at ordinary temperatures. A weighed quantity of the metal in plates was placed in a basket of platinum gauze, suspended in the liquid, and allowed to remain for four minutes. It was then reweighed. The heat of combustion of indium was found to be:—

	I.	II.	Mean.
For a gram	1,044·4	1,044·9	1,044·6
For an equivalent..	37,493	37,512	37,502

* Compt. rend., lxxii, 858—862, and lxxiii, 108—111.

As cadmium is not attacked by either sulphuric or hydrochloric acid, even in contact with platinum, iodic acid was resorted to. The reaction is simple: for although iodine is liberated in presence of an excess of the metal, no iodide is formed, since that body in contact with iodic acid is immediately converted into iodate and free iodine. The heat of combustion of cadmium as obtained by this method was:—

	I.	II.	Mean.
For a gram	277·3	264·9	271·1
For an equivalent ..	15,527	14,835	15,231

The following table shows the maximum and minimum values of the heat of combustion of the four metals examined:—

			Magnesium.	Zinc.	Indium.	Cadmium.
Heat of Combustion.	For a gram	Max.	6073·9	1391·2	1044·6	275·5
		Min.	5944·9	1324·3	,,	271·1
	For an equivalent	Max.	72890	45401	37502	15506
		Min.	69222	43125	,,	15231

Comparing the preceding numbers with the principal physical properties of these metals, we arrive at some interesting relations. Magnesium burns vividly in air, zinc not so energetically, indium with some difficulty, while cadmium gives a flame so pale as scarcely to be visible. Three causes modify these phenomena: the physical state of the oxide, the temperature of combustion, and the volatility of the metal. The influence of the first of these causes has been studied by Caron; the second depends on the amount of heat developed in the combustion. This diminishes from magnesium to cadmium, and explains, without reference to the physical state of the oxide, the decreasing luminosity of the flames of the successive metals. In the third place, the greater the volatility of the metal, the more extended will be the flame. This volatility increases from magnesium to cadmium, and accounts for the fact that the first burns as a luminous point, and the last with a pale and attenuated flame.

Magnesium decomposes pure water at any temperature above 70°, and its vapour at a lower temperature; zinc, although unaffected by water, is easily oxidised in steam, while cadmium requires a red heat to accomplish the separation of the oxygen. In cases, therefore, where the heat of combustion of a metal is small, as with cadmium, water may still be decomposed, provided it is previously heated to a sufficiently high temperature.

Again, hydrogen reduces cadmium oxide at about 400°, and indium oxide at a red heat; but the reduction of zinc oxide only commences

at a very high temperature in a rapid stream of gas, and magnesia shows traces only of decomposition in a gas furnace, when oxygen predominates. It would seem from this that the reduction of a metallic oxide by hydrogen is easier, the less the heat of combustion of the metal.

The action of carbon and carbonic oxide is analogous to that of hydrogen.

The following table shows the parallelism existing between the different physical and chemical properties of the four metals considered:—

Physical properties.	Magnesium.	Zinc.	Indium.	Cadmium.
Density	1·75	6·8 to 7·2	7·15	8·6 to 8·7
Equivalent	12	33	35·9	56
Specific heat	0·2633	0·0955	0·0877 (by theory)	0·0567
Product of specific heat and equivalent	3·16	3·15	3·16	3·17
Temperature of fusion	About 500°	About 400°	..	About 315°
Temperature of volatilization	About 1100°	1040°	Red heat	860°
Heat of combustion	72890	44258	37502	15231
Colour of the oxides	White	White or light yellow	Rich yellow	Orange or black

S. W.

On the Freezing of Water. By M. Boussingault.*

A cylinder of steel 46 centims. long, was bored to a depth of 24 centimetres, the width of the boring being 1·3 centims., the thickness of the wall was 8 mm.; the cylinder was also fitted with a cap, which could be screwed on perfectly tight. A small ball of iron was placed in the interior, so as to indicate the state of the water inside, whether frozen or not. The cylinder was filled with distilled water at 4° C., and the vessel closed; it was then exposed to a temperature of − 24°, when the mobility of the iron ball proved that the water was still liquid. It was opened at − 10°, and immediately on the removal of the pressure the water solidified. In a second experiment the water was exposed to a temperature of − 18° with a similar result. A. P.

* Comp rend., lxxiii, 77.

On the Action of Electricity on the Coloured Tissues of Plants. By M. BECQUEREL.*

THIS subject has already been investigated by Kabsch and Kühne.† Becquerel takes exception to their results, because in their experiments a chemical action took place, besides the simple action of the electricity. They used an induction apparatus, the electrodes of which were in contact with the substance under examination, such as a petal; an alkali and an acid were thus formed, which acted on the colour of the petal. Kabsch appeared to attribute the effects of decoloration to ozone, but Becquerel proves that this is not the case. The apparatus used by the latter consists of a universal discharger, furnished with two small balls of platinum at the extremities of the movable arms; these are placed on a band of moistened paper spread on a glass plate; a petal of a flower, such as the *Papaver orientalis*, is moistened and placed on the paper; one arm of the discharger is connected with the earth, and the other with an insulated ball standing near an ordinary electrical machine. After the passage of a few sparks, the parts of the petal nearest the platinum balls become colourless; if the discharge is then stopped, the white spots gradually spread over its surface; if, however, the petal be placed in water, this takes a violet tint, the former becoming colourless. A more uniform result is obtained by placing the petal between two long bands of moistened filter paper, and placing the two balls between the surfaces, at a definite distance from the object.

Red and blue flowers are much more sensitive to this action than yellow flowers; the colours of the former may be due to liquids, whilst the yellow is probably due to solid granules. Leaves when acted on by the spark appear at first to be unchanged. Some time after the cessation of the sparks, the parts acted on gradually become brown, sometimes appearing like a dead leaf when the current is long continued. The leaves of the *Bigonia discolor*, which are red on one face and green on the other, present a remarkable effect, the green part becoming sensibly red, and the red, green. In some experiments, instead of a simple spark, a pile was used composed of six elements of nitric acid and amalgamated zinc, which gave precisely similar results. These effects are not produced by ozone, as some of the experiments were made in tubes filled with hydrogen or carbonic anhydride. Similar effects are produced by the action of boiling water; thus, if the petal of a red poppy be placed in boiling water for a few seconds, the colour changes; if it is now placed in cold water, the violet colour dissolves out, and leaves it colourless; the action on the Begonia is the same as that of electricity. The electricity from an excited glass tube can be

* Compt. rend., lxxiii, 65—77. † Botan. Zeit., 1861, 362.

used to produce similar results; the small quantity of electricity required seems to exclude the calorific origin of the change. Neither is it an electro-chemical effect, inasmuch as the results are similar at both the balls of the discharger. It seems, therefore, to be a peculiar action of the electricity; it may be imagined that at the instant of the discharge, a series of decompositions and recompositions of the electric fluid occurs, and that the tissue of the cells is altered, which allows the coloured liquid to filter through when placed in cold water.

If the petal of the poppy be examined by the microscope, the tissue is found unaltered, the appearance of the cells being precisely the same as originally. A leaf of ivy, which had been browned by the action of the spark, presented on its surface a number of small ruptures; the chlorophyll did not appear to be much acted on.

Electric discharges, strong or weak, appear, therefore, to produce three distinct actions on the colours of leaves and flowers. 1. An action by which the electrified parts allow the colouring matters which are in solution in the cells to filter into cold water. 2. A direct decolorising effect on red and blue colouring matters which are in the liquid state in the cells. 3. An infiltration or a transport of colouring matters in the interior of the organs electrified, as in the case of the Begonia. Somewhat similar effects may take place in the animal body when exposed to the action of electricity.

A. P.

On a Simple Gas-washing and Gas-absorption Apparatus. By H. Fleck.*

The apparatus described is very simple and handy; it consists of an ordinary U-shaped tube fitted with two corks; through each of these two glass tubes pass, bent at right angles, one of them extending below the surface of a liquid, with which the U-tube is partially filled, while the other only extends through the cork; this latter tube is connected with the long tube which passes into the liquid at the other limb of the U-tube, thus securing the passage of a gas twice through the same liquid. The author details a number of cases in which this piece of apparatus may be used; these, however, will readily suggest themselves.

A. P.

On the Internal Motion of Gases. By O. E. Meyer. (Pogg. Ann. cxliii, 14—26.)

* J. pr. Chem. [2], iii, 349—351.

Melting of Leaden Bullets by Impact on Iron Plates. By E. HAGENBACH. (Pogg. Ann. clxiii, 153.)

Remarks on Thomsen's Experiments on the Specific Heat of Aqueous Solutions. By A. WÜLLNER. (Pogg. Ann. cxliii, 156.)

On the Elasticity of Caoutchouc. (Pogg. Ann. cxliii, 88—101.)

On Fluorescence. By E. LOMMEL. (Pogg. Ann. cxliii, 26—52.)

On Spectroscopic Phenomena produced by Dispersion. By F. KOHLRAUSCH. (Pogg. Ann. cxliii, 144.)

New Method of Spectroscopic Observation of the Sun. By. P. SECCHI. (Pogg. Ann. cxliii, 154.)

On the Density of Elements compared with that of their Oxides. By H. LUDWIG. (Deut. Chem. Ges. Ber. iv, 538—547.)

Inorganic Chemistry.

On the Decomposition of Carbonic Oxide by the Combined Action of Metallic Iron and its Oxides. By L. GRUNER.*

GRUNER has studied the action of iron and its oxides upon carbonic oxide at a temperature of 300°—400°; the results which he has obtained agree for the most part with those obtained by Lowthian Bell,† although there are some points on which they differ. The present communication contains the conclusions which the author has drawn from a series of experiments with carbonic oxide, both pure and mixed with nitrogen or carbonic anhydride, upon pure iron and on various iron ores. When pure and dry carbonic oxide is passed over metallic iron at 300°—400°, scarcely any deposit of carbon takes place; Gruner believes that if the surface of the iron were perfectly free from oxide no deposition would take place. When carbonic oxide is passed over oxide of iron, the oxide is reduced at the surface to metallic iron,

* Compt. rend., lxxiii, 28—32.

† Journal of the Iron and Steel Institute, February, 1871.

and a deposit of carbon is formed. Carbonic oxide mixed with a small quantity of carbonic anhydride or oxygen, and passed over metallic iron at this temperature, deposits pulverulent carbon on the surface of the iron. The carbon which is deposited in these experiments contains metallic iron, sometimes amounting to 5—7 per cent., and some oxides of iron, for the most part magnetic. The reactions which take place between carbonic oxide and protoxide of iron in the presence of small quantities of carbonic anhydride for the deposit of carbon, may be supposed to be—

$$3FeO + CO = Fe_3O_4 + C; \text{ and again,}$$
$$Fe_3O_4 + CO = 3FeO + CO_2.$$

Carbonic anhydride always acts as an oxidizing agent towards iron; at the temperature of 100°—400° this action is but feeble, and produces only small quantities of the sesquioxide, magnetic oxide, and protoxide of iron, neither of which is accompanied by a deposit of carbon. If in the experiments which yield carbon the temperature is raised to redness, the depositing immediately stops, and if there is protoxide of iron present it is again burnt.

Looking to the theory of the blast-furnace, it is remarkable that carbon should be deposited in the upper part of the furnace, and by its intimate mixture with the protoxide of iron should facilitate the reduction of the ore. The presence of iron in the deposited carbon makes the supposition possible, that natural graphite containing iron may have originated in a similar manner.

A. P.

Preparation and Purification of Carbon Bisulphide. By TH. SIDOT.*

THE author has observed that in the manufacture of carbon bisulphide the yield depends mainly upon the temperature employed. His experiments consisted in passing a known weight (40 grams) of sulphur, in the form of vapour, over 10 grams of charcoal contained in a porcelain tube heated to various temperatures. The numbers given below represent the mean results of three experiments at each of the temperatures mentioned.

1.	At a dull-red heat,		5	grams of carbon	gave	17	grams of carbon bisulphide.
2.	,,	red heat	6·3	,,	,,	29	,,	,,
3.	,,	bright-red ,,	7·5	,,	,,	19	,,	,,

These numbers show clearly that, in order to obtain the maximum yield, a red heat should be employed, but that it should by no means

* J. Pharm. [4], xiii, 239—242.

be exceeded. In practice the variations in the yield of carbon bisulphide are attributed to loss, to imperfections in apparatus, and chiefly to temperature, which is always considered to be too low. The above result, which it may be useful to manufacturers to know, is due to the fact already pointed out by Berthelot, that carbon bisulphide undergoes decomposition the more completely the higher the temperature to which it is exposed. It behaves in presence of charcoal exactly like the carbon oxide in Deville's dissociation experiments, undergoing simple decomposition, and the liberated carbon being deposited upon the heated charcoal. The author has made a series of comparative experiments at different temperatures, the results of which show that decomposition takes place to some extent even at a dull red heat, but that it goes on much more rapidly at higher temperatures; 150 c.c. of carbon bisulphide were completely decomposed by passing six times over 10 grams of charcoal heated to bright redness in a porcelain tube.

To purify carbon bisulphide, the author first distils, and then agitates it with mercury, till it ceases to blacken the brilliant surface of the metal. This latter operation is performed as follows:—500 grams of the bisulphide, and about the same weight of mercury, are introduced into a bottle of 500 c.c. capacity, which is then agitated for some time. The sulphide formed is readily removed by filtration, and the mercury separated by means of a funnel. The two liquids are then returned to the bottle, and the agitation is renewed, until the bright surface of the mercury is no longer tarnished. Carbon bisulphide thus purified is completely free from the fetid smell which it generally possesses, and has a pure ethereal odour. It is not affected by contact with mercury for any length of time.

J. R.

On the Solubility of Carbon Bisulphide in Alcohol. By C. Tuchschmidt and O. Follenius.*

It is not correct, as generally stated, that carbon bisulphide mixes in all proportions with common strong spirit, which indeed takes up the less of it the more water it contains. It is only with absolute alcohol that carbon bisulphide is miscible in all proportions. These facts afford a means for testing the strength of alcohol, as the point of saturation can be very exactly determined, one drop of bisulphide in excess producing a strong milky turbidity. The only precaution to be attended to is to work at a temperature above 15°, because below that point the solubility decreases rapidly with the temperature, whilst above it the solubility remains nearly constant. Thus, when a saturated solution

* Deut. Chem. Ges. Ber. iv, 583—585.

is cooled down from + 15° to − 12°, about one-half of the bisulphide separates out; at − 10° one-third, and at + 10° about one-fifth.

The following results were obtained, 10 cub. cent. of alcohol were used in each experiment, the temperature being 17°:—

Percentage of Alcohol by weight.

98·5	98·15	96·95	93·54	91·37	84·12	70·02	48·40	47·90

Cub. cent. of CS_2 dissolved.

18·20	13·20	10·00	7·00	5·00	3·00	2·00	0·2	0

By inserting these values in a system of co-ordinates, a curve having the following formula is obtained:—

$$y = \frac{1}{x}\left(s - \frac{c}{x + b}\right)$$

$$x = \frac{(s - yb) + \sqrt{(s + yb)^2 + 4yc}}{2\,y}$$

when $a = 1{\cdot}065$, $b = 0{\cdot}58$, and $c = 0{\cdot}592$.

On calculating from these equations, y, or the quantity of bisulphide in cbc. dissolved in 10 cbc. of alcohol of x per cent. by weight, the numbers found agree almost exactly with those found by experiment. On the other hand we can easily calculate x, when we know how much bisulphide dissolves in 10 cbc. of the alcohol to be tested. Alcohol which mixes in all proportions with bisulphide may be considered as anhydrous.

C. S.

On Hydrated Calcium Carbonate. By C. Rammelsberg.*

Small crystals attached to confervæ from a pond were found to be the hydrate with 5 mol. of water, which Pelouze had obtained from a solution of lime in sugar, and which Salm-Horstmar afterwards observed in a water-pipe. This compound is distinguished by losing its water above 15° even when immersed in water.

C. S.

Note on Potassic Iodochromate. By P. Guyot.†

When potassic chromate is treated with colourless hydriodic acid, a salt is obtained which on analysis gives the formula $CrO_2 \left\{ \begin{matrix} OK \\ I \end{matrix} \right.$. It is therefore potassic iodochromate. It is a garnet-red crystalline salt; if

* Deut. Chem. Ges. Ber., iv, 469. † Compt. rend., lxxiii, 46—47.

it contains an excess of iodine it may have a brown tint, but on exposure to the air it gradually assumes its normal colour.

It is decomposed in the presence of water into hydriodic acid and potassic dichromate. When heated it gives off iodine copiously, on boiling it with hydriodic acid more iodine is given off, potassic iodide and chromium sesqui-iodide remaining behind. E. T. C.

On some Substances Crystallised from Microcosmic Salt and from Borax. By A. Knop.*

This paper, which is a continuation of a former one on titanic acid,† contains the author's investigations of the compounds of tin and zirconium obtained by Wunder ‡ by crystallisation from the above-mentioned fluxes, and also those of niobium. The flux was removed from the crystals formed in microcosmic salt after two hours' fusion at a white heat, by means of dilute hydrochloric or sulphuric acid, and, after washing away the amorphous portion, the crystals of different sizes were separated from one another by mechanical means, the larger being used for optical examination and for the determination of their crystalline form, the smaller for the specific gravity and for analysis. The crystals in almost every case consisted of right-angled parallelopipeds which distinctly affected polarised light. All those from fused borax were oxides, and were recognised partly by the identity of their forms with those of the natural oxides or by their pleomorphism, and partly by direct analysis and by a determination of their specific gravities. Since the very uniform temperature of the Perrot furnace was unfavourable to the production of currents in the flux when borax was employed, it was found that much better crystals could be obtained in a platinum crucible heated by a blowpipe flame. A high temperature was maintained in the first instance until the flux had become saturated with the substance under examination, and then by directing the flame so as to heat one side of the crucible more than the other, currents were set up in the fused mass which favoured the deposition of well-formed crystals. These were afterwards separated in a manner similar to that employed in the case of microcosmic salt. In order to watch the progress of the crystallisation, a platinum wire bent into a ring at one end was occasionally dipped into the fused mass, and the thin film of borax formed on withdrawing it examined as a microscopic object.

* Ann. Ch. Pharm., clix, 36—58.

† Ann. Ch. Pharm., clvii, 363, and this volume, p. 200.

‡ Journ. f. prak. Chem. [2], ii, 206.

I. Crystallisations from Microcosmic Salt.

a. *Phosphostannic Acid.*—When a large excess of stannic acid was added to the fused microcosmic salt, pyramidal forms were obtained which had a striking resemblance to those of anatase. A microgoniometric measurement gave 136° 36′ as the basal angle of the quadratic pyramid. The crystals were very large compared with the parallelopipedal form of phosphostannic acid, and measured $\frac{1}{10}$ mm. along the principal axis, whilst the ordinary forms were only $\frac{1}{350}$ mm. The pyramids were translucent and rough, and had a specific gravity of 3·98 and 3·87, whilst the cubic forms were transparent and smooth and had a specific gravity of 3·61, tinstone having a specific gravity of 6·0 to 7·1. The crystals were analysed by fusing them with sodium carbonate and sulphur, thus separating the tin as sulphide, which was afterwards weighed as stannic acid, the phosphoric acid being determined in the sodic flux in the usual way. As the analyses varied considerably amongst themselves, and moreover, the sum of the percentages of the phosphoric acid and of the stannic acid was in some instances considerably in defect of 100, especially in the case of pyramidal crystals, the author was inclined to suspect the presence of soda, which he ultimately succeeded in detecting and estimating. As the amounts of soda, phosphoric acid, and stannic acid present bore no relation to one another, showing that it was not a homogeneous chemical compound, the crystals were fused at a high temperature with glacial phosphoric acid, and, after the careful removal of the flux, again submitted to analysis. The compound crystallising in the pyramidal form was then found to have the composition $2SnO_2,P_2O_5$, and was therefore bibasic phosphostannic acid, and the cubic SnO_2,P_2O_5 monobasic phosphostannic acid. An analysis of another preparation crystallising in the cubic form indicated an approach to the composition $3SnO_2,P_2O_5$. From these results the author infers that mixtures of mono-, bi-, and tri-basic phosphostannic acid are formed, varying according to the relative proportions of the materials originally employed.

b. *Phosphozirconic Acid.*—The zirconic acid employed in these experiments was prepared by Wöhler's method* from zircons obtained near Asheville, North Carolina. The finely pulverised mineral was fused with potassium carbonate, and the product, after being exhausted with water, was treated with an excess of hydrochloric acid and evaporated to dryness. Water then dissolved but a portion of the substance, the residue becoming soluble only after having been treated with sulphuric acid. This behaviour of the zircons renders it probable that what is known as zirconia consists of two different substances. Svanberg†

* Prakto. Uebungen in. d. chem. Anal. Göttingen, 1853, 108.

† Berzelius Jahresb., xxv (1846), 149.

named the element contained in the soluble chloride, *norium*, and described the differences which he observed between its reactions and those of zirconium, which were confirmed by Sjögren.* Berzelius, and subsequently Hermann,† on the contrary, denied the existence of norium. The author, after referring to the jargonium of Sorby and Church,‡ which was subsequently investigated by Forbes,§ states that he could not observe any absorption-spectrum in the zircons employed by him corresponding to that assigned to jargonium, and the chemical reactions of the soluble chloride agreed rather with those ascribed to norium by Svanberg than to those of jargonium. Without expressing a decided opinion as to whether the substances are different or not, in order to avoid periphrasis, he calls the precipitate formed by the addition of ammonia to a solution of the soluble chloride *noria*, and that obtained from the insoluble portion *zirconia*. When these earths were separately fused with microcosmic salt in the way previously described, a white crystalline powder was obtained, consisting in each case of microscopic right-angled parallelopipeds. The crystals were colourless, smooth, and transparent, and acted much more feebly on polarised light than the titanic and stannic compounds. The specific gravity of the zirconic compound was 3·12, that of the noric compound 3·14. The analysis of these crystals showed that, like the stannic compounds, they contained soda, which was removed by fusion with glacial phosphoric acid. The formula of the noric compound was then found to approximate very nearly to $NrO_2.P_2O_5$.

c. *Phosphoniobic Acid.*—Niobic acid dissolves in the phosphatic flux in large quantity, but as the author did not succeed in obtaining anything but amorphous products on treating the flux with dilute acid, he concluded that phosphoniobic acid is uncrystallisable.

II. Crystallisations from Borax.

a. *Stannic Acid.*—The properties of this oxide, when crystallised from borax, have been so accurately described by Wunder (*loc. cit.*), that the author has scarcely anything to add, although he has observed that with a mixture of microcosmic salt and borax in which there is an excess of the phosphate, a compound ($2SnO_2.P_2O_5$) crystallises out in the pyramidal form; that the addition of a large excess of borax to the flux causes the withdrawal of one-half of the stannic acid, forming the cubic compound SnO_2,P_2O_5, and a still greater excess of borax decomposes this, the acid crystallising out in the rutile form.

b. *Zirconia and Noria.*—On account of the great similarity of the crystalline forms of the phosphoric acid compounds, there was no

* Pogg. Ann., iii. 1853, 465.
† J. pr. Chem., xxxi, 75.
‡ Chem. News, 1869, 121 and 205.
§ Chem. News, 1869, 277.

chance of distinguishing zirconia and noria by a morphological examination of these compounds, but as, on the contrary, the oxides have considerable variety of form, the author hoped to be able by this means to find points of distinction between these earths. As the addition of borax to the stannic phosphate, when fused with a mixture of borax and microcosmic salt, decomposed it with formation of crystallised stannic oxide, it was to be hoped that the corresponding zirconium and norium compounds would be similarly acted upon. On making comparative experiments, it was found that the zirconia phosphate was unchanged, whilst the noria compound had undergone partial decomposition, a few large, irregularly formed plates being mingled with the original cubic crystals. These plates were aggregated into regular hexagonal star forms, which rivalled in beauty those of snow crystals. This result did not invite further investigation, and the author does not believe that the difference in behaviour between the zirconia and noria necessarily indicates a specific difference between them. The oxides, however, were obtained in a crystalline state from melted borax.

α. Zirconic Acid.—After the fusion with borax and treatment with dilute acid, a crystalline residue was left, in which moderately large, well formed, transparent crystals, having numerous faces, were observed. At the first glance they gave the impression of the rhombic combination of heavy spar. A vertical prism, a pinacoïd parallel to the principal axis, and two domes could be distinctly recognised, and the goniometric measurements made showed it to be the same rhombic combination as that which is peculiar to brookite. For this a (principal axis) : b : c = 1·162 : 1 : 1·1883. The angle of the brachydome in the principal axis : $\overset{\circ}{P}\infty$: $\overset{\circ}{P}\infty$ was 81° 26′; of the macrodome $\overline{P}\infty$: $\overline{P}\infty$ 91° 18′. The zirconic acid crystals may be represented by the combination $\infty\overline{P}\infty . \infty P . \overset{\circ}{P}\infty . \overline{P}\infty$. The largest crystal was $\frac{12}{36}$ mm. in length, and $\frac{4}{36}$ mm. in breadth, and the specific gravity, 5·42. Sjörgren gives 5·5 for zirconia; Nordenskiöld, 5·742.

β. Noria.—The crystals prepared for microscopic examination were evidently different from those of zirconia, being much smaller, namely, about $\frac{1}{16}$th the size. Those obtained in the blowpipe flame by the method already described were thick quadratic prisms, with pyramidal summits, similar to the crystals of zircon, but in some individuals indications of other faces could be observed. From measurements taken, the principal axis was reckoned at 1·19 or 1·2, whilst for zircon and rutile it is only 0·64, or about one-half. Nordenskiöld* measured crystals of zirconia obtained from katapleüte which were similar in habitus to noria crystals, a being = 1·0061. The specific gravity of

* Pogg. Ann., xxiv, 625.

the noria crystals was found to be 5·52. A microscopic examination of preparations of the crystals of zirconia and noria obtained by dipping a ring of platinum wire into the boracic flux showed that the crystallisation of the two substances was identical, consisting apparently of a combination of four-sided rectangular prisms, interspersed, however, with isolated, short, thick prisms, with pyramidal summits. On dissolving out the flux, however, and observing the crystalline residue, the network had broken up into the rhombic crystals beforementioned as resembling brookite. All the forms being observed, both in zirconia and noria, it was evident that they could not be distinguished by their crystalline form. Considering this, and the comparative inaccuracy of the microgoniometric measurements of such small crystals, the author is of opinion that microscopic observations of the isomorphism or pleomorphism of crystals do not authorise us in pronouncing two substances to be identical or different. Not only do the above described observations render it more probable that zirconium and norium are identical, but the properties of their double salts tend to the same conclusion. It is true, as Svanberg has observed, that the zircon earth yields two double salts with potassium sulphate, one of which is soluble, and the other insoluble, but by evaporating the solution of the former to dryness, and fusing the residue with acid potassium sulphate, it again separates on being treated with water into a soluble and an insoluble portion. In order definitely to ascertain the identity or non-identity of the two substances under consideration, it would be necessary to institute an extensive comparative examination of the crystalline forms of their compounds.

γ. *Niobic Acid.*—Nordenskiöld* obtained crystals of niobic acid from fused borax, which had a specific gravity of 5·20 and 5·48, affected polarised light, and were considered by him to belong to the rhombic system. The author obtained distinct crystallisations in the blowpipe flame, which agreed with the trigonal growths of potassium chloride from its aqueous solutions. By continuing the heat these became aggregated into regular, well formed cubes, the largest measuring about $\frac{1}{5}$ mm. on the side. They were transparent and glistening, and under the microscope appeared of a pale violet colour. Their specific gravity was 4·31; Marignac found for niobic acid 4·37 to 4·53. As the crystals affect polarised light, the author does not believe that they belong to the monometric system, although it is possible, as in the case of potassium chloride, that the trigonal growths of cubes form a lamellar system, and thus cause a lamellar polarization of light, in which the molecular constitution of the substance takes no part.

C. E. G.

* Pogg. Ann., xxiv, 626.

Further Researches on the Compounds of Ilmenium and Niobium, and on the Constitution of Niobium Compounds. By R. HERMANN (J. pr. Chem. [2] iii, 373—427).

Mineralogical Chemistry.

The Granulytes of Saxony. By A. STELZNER.*

THE author gives the results of the analysis of specimens of rocks obtained from the following localities:—I. Normal granulyte from Neudörfchen, near Mittweida. II. The same from the Klaumühle at Limbach. III. The same from Röhrsdorf. IV. Gneissoïd granulyte from Steina, near Hartha. V. The same from Harmannsdorf, near Burgstädt. VI. Normal granulyte from Penig. VII. Trap-granulyte from Ringethal, near Mittweida. VIII. The same from the Klaumühle at Limbach, interstratified in sharply-defined layers with II. IX. The same from Harmannsdorf, near Burgstädt. X. Compact gabbro, from Böhringen. XI. Medium-granular gabbro, from Mahlitzsch, near Rosswein. XII. Hypersthenite from the Höllenmühle, near Penig.

	SiO_2.	Al_2O_3.	FeO.	MnO.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	SO_3.	CO_2	
I.....	75·80	12·09	2·18	..	0·38	1·45	4·27	2·72	0·63	..	..	99·52
II. ..	75·46	12·09	3·38	..	0·66	1·22	3·96	2·46	0·63	..	..	99·86
III. ..	75·46	13·45	2·22	..	0·42	0·73	3·65	2·48	1·11	..	..	99·51
IV. ..	74·60	12·84	2·39	..	0·23	0·73	5·82	2·39	1·02	..	..	100·02
V. ..	73·47	11·07	5·33	..	0·73	1·81	3·76	2·89	0·77	..	..	99·83
VI. ..	72·97	12·69	4·10	..	0·63	2·33	3·46	3·16	0·58	..	..	99·92
VII...	56·92	14·63	12·14	..	6·10	8·56	..	..	1·46	..	..	99·81
VIII .	49·95	13·95	15·97	..	7·91	10·37	..	..	1·67	..	..	99·82
IX. ..	49·73	12·81	16·75	..	7·41	11·13	..	..	1·94	..	..	99·79
X. ..	50·54	12·90	13·01	2·28	6·85	10·95	0·82	2·03	1·08	..	..	100·46
XI. ..	49·45	19·28	11·93	trace	4·18	9·86	..	2·59	2·35	0·22	..	99·86
XII...	48·85	19·45	8·15	trace	3·85	17·51	..	..	1·03	..	0·82	99·66

The normal, schistose, or granular granulytes, the weisstein enclosing garnet or cyanite, with which are also included those varieties having gneiss-like characters through the mica they contain, and the finely-granular greenish-black trap-granulytes, are readily distinguished. The first kind are rich in silica and alkalies, but deficient in iron protoxide, the trap-granulytes being more basic, containing considerable

* Jahrbuch für Mineralogie, 1871, 244.

amounts of lime and magnesia in place of alkalies, and an abundance of magnetite. It was found, on examining sections under the microscope, that the normal weissteins are almost always composed of quartz and orthoclase, the trap-granulytes of quartz, triclinic felspar, magnetite, and a green micaceous mineral. In the trap-granulytes enclosing garnet, peculiar grouping of the constituent minerals was remarked. The granules of garnet are embedded in a zone of felspar, and in some varieties the mica and magnetite lying in the immediate neighbourhood of the garnet, have a quite peculiar radial arrangement. The author holds that the various granulytes, though exhibiting chemical and mineralogical differences, are members of one and the same rock-formation, and that granulyte is a metamorphic, and not an eruptive rock.

W. F.

The Geology of Meteorites. By S. MEUNIER (Moniteur Scientifique, xiii, 97—119).

Organic Chemistry.

On Propylene Compounds. By L. HENRY.*

BY slowly adding propylene oxide to well-cooled fuming nitric acid, and pouring the solution in water, *propylene dinitrin*, $C_3H_6(NO_3)_2$, separates as an oily, colourless liquid. By using amylene oxide, the corresponding dinitrin was also obtained. These compounds will be fully described in a further communication.

C. S.

Preparation and Properties of Propylic and Butylic Chlorides. By IS. PIERRE and ED. PUCHOT.†

Propylic chloride, C_6H_7Cl. Two methods of preparation were adopted.

The first consisted in saturating propylic alcohol (which then contains in every 100 grm. 58 grm. of hydrochloric acid) with hydrochloric acid, and distilling the acid mixture thus produced. In the second, which the authors prefer, perchloride of phosphorus was added slowly to propylic alcohol, keeping the temperature of the mixture as low as possible. In one operation 240 grams were taken to 168 grams of the perchloride.

* Deut. Chem. Ges. Ber. iv, 602—604. † Compt. rend., lxxii, 832—838.

When all the perchloride had been added, the mixture was distilled. The portion collected below 75° was principally propylic chloride. It was freed from hydrochloric acid and propylic alcohol by washing with water, dried with chloride of calcium, and purified by rectification. The authors obtained 180 grams of nearly pure chloride from 480 grams of the alcohol.

Perfectly pure propylic chloride is a limpid, colourless liquid, with a slightly alliaceous, though sweet odour. It boils at 46·5°. Its specific gravity is 0·9156 at 0°, 0·8918 at 19·75°, 0·8671 at 39°.

If the distillation of the residue in the retort is continued after the propylic chloride has been driven over, the propylic alcohol which has not been acted on comes over first at about 90°. On raising the temperature further, a point is reached at which the residue begins to froth up, some inflammable gas being at the same time given off; if the lamp is withdrawn when this evolution of gas appears to cease, a vigorous reaction sets in with violent effervescence, and some quantity of a limpid ethereal liquid distils over spontaneously. Hydrated phosphoric acid and a light amber-coloured liquid remain behind in the retort. The above-mentioned gas combines in diffused daylight with chlorine, the combination being attended with evolution of heat and a rapid contraction of volume, whilst a liquid closely resembling Dutch liquid is formed.

Butylic chloride, C_8H_9Cl. The methods of preparing this body, and the reactions observed during the process, are almost exactly similar to those described in the case of propylic chloride. The authors prepared altogether about 650 grams of butylic chloride. It is a very mobile, perfectly limpid liquid, with an ethereal odour, agreeable, though slightly alliaceous; boils at 60° under the ordinary pressure.

Its specific gravity is 0·8953 at 0°, 0·8651 at 27·8°, 0·8281 at 59°.

The authors give the following table, showing the specific volumes of propylic and butylic chlorides at equal distances from their boiling points:—

Distance in degrees centigrade from the boiling point.	Specific volume.	
	Propylic chloride.	Butylic chloride.
0	1·0000	1·0000
10	0·9850	0·9848
20	0·9708	0·9705
30	0·9572	0·9570
40	0·9443	0·9443
50	0·9322	0·9322
60	0·9209	0·9208
70	0·9103	0·9101

E. T. C.

Conversion of Succinic Acid into the Corresponding Diatomic Alcohol. By A. SAYTZEFF.*

BY the action of sodium amalgam on a mixture of succinyl chloride and acetic acid, the author has obtained a butylic glycol, which appears to be the true homologue of ethylic glycol, viz. :—

$$CH_2OH—CH_2—CH_2—CH_2OH.$$

On the Artificial Production of Dulcite. By G. BOUCHARDAT.†

THE relation existing between the hexatomic alcohol mannite and the saccharine bodies obtained by the action of dilute acids on cane-sugar, is well known; all these different substances, when oxidsed, yield saccharic acid and otherwise identical products. Linnemann succeeded in definitely establishing their relation by directly converting inverted cane-sugar into mannite by hydrogenation:

$$C_6H_{12}O_6 + H_2 = C_6H_{14}O_6.$$

Berthelot first pointed out that a similar relation probably exists between inverted sugar of milk, galactose, and the hexatomic alcohol dulcite, or an isomeride of dulcite, all of which yield mucic acid amongst their products of oxidation. The author has succeeded in proving this experimentally. An aqueous solution of galactose was acted upon by 2·5 per cent. sodium-amalgam, the liquid being neutralised by dilute sulphuric acid from time to time; at the termination of the reaction, the liquid was exactly neutralised by acid, and the greater part of the sodium sulphate removed by crystallisation, the last portions by mixing the solution with twice its volume of strong alcohol. It was then filtered and concentrated to the consistence of a syrup. After some time, small crystalline warty groups separated out; these were removed and drained on filter-paper; a further quantity of crystals was deposited on allowing the liquid to stand. The substance thus obtained is readily purified by recrystallisation from water; on analysis it gave 39·3 and 39·1 per cent. of carbon, 7·85 and 7·9 per cent. of hydrogen, the theoretical numbers for dulcite being 39·5 per cent. carbon, and 7·7 per cent. hydrogen. The crystals are gritty between the teeth, but scarcely saccharine in taste; they are not fermentable in contact with beer-yeast; their melting point was found to be 187°, pure dulcite melting at 188·5°; they are very slightly soluble in strong alcohol; 100 parts of water at 21° dissolve 4·1 parts, pure dulcite dissolving to the extent of 3·6 to 3·7 parts, the difference being, no doubt, due to slight impurity. The substance in solution has no

* J. p. pr. Chem. [2], iii, 427. † Compt. rend., lxxiii, 199.

appreciable action on a ray of polarised light. It is not browned by boiling with potash, nor does it reduce a cupro-potassic solution. On treating it with nitric acid diluted with four times its volume of water, crystals of mucic acid were obtained. There seems then to be little doubt but that the body obtained is identical with dulcite, first extracted from the manna of Madagascar, and since found in *Melampyrum nemorosum*. H. E. A.

Dambonite. By P. CHAMPION.*

DAMBONITE in presence of a mixture of sulphuric and nitric acids, is transformed into a thick, translucent, gummy substance, which in water precipitates in the form of flakes. This precipitate carefully washed and dissolved in boiling alcohol deposits crystals of nitrated dambonite. This body is insoluble in water, and detonates when struck.

J. B.

Compounds of Erythrite. By P. CHAMPION.†

Erythritic Dibromhydrin.—When erythrite is treated with a saturated solution of hydrobromic acid in a sealed tube at the temperature of 110° for three hours, a brown liquid is obtained, which when evaporated in the water-bath and redissolved in boiling ether, deposits crystals of erythritic dibromhydrin. These crystals, after purification, have the composition 19·34 C., 3·39 H., 13·27 O., 64 Br., corresponding with the formula $C_4H_8Br_2O_2$, or $(C_4H_6)_{iv}Br_2(OH)_2$. This body is insoluble in water, slightly volatile at 100°, melts at 130°, and forms a crystalline mass on cooling. In its composition and properties it resembles the erythritic dichlorhydrin prepared by De Luynes.

Erythritic Dinitrodibromhydrin. When erythritic dibromhydrin in powder is introduced into a cold mixture of 1 part fuming nitric acid and 2 parts concentrated sulphuric acid, the temperature slowly rises, and if after a contact of some minutes the whole be poured into cold water, a white flaky precipitate is formed, which, after being washed and dissolved in boiling alcohol, deposits long white flexible needles, having the composition 13·71 C., 2·00 H., 28·00 O., 47·39 Br., 8·90 N., corresponding to the formula $C_4H_6Br_2O_2(NO_2)_2$. This body is insoluble in water; melts at 75°; does not detonate when struck, like nitro-erythrite; is decomposed by heat, producing yellow fumes. A boiling solution of potash changes it, the liquid becoming brown, and a nitrate being formed.

Erythritic Dinitrodichlorhydrin. This body, like the preceding, is obtained by causing a mixture of nitric and sulphuric acids to react

* Compt. rend., lxxiii, 114. † Ibid.

upon erythritic dichlorhydrin. Its composition is 19·27 C., 2·41 H., 38·56 O., 28·52 Cl., 11·24 N., corresponding to the formula $C_4H_6Cl_2O_2(NO_2)_2$. It crystallises easily from alcohol, melts at 60°, and has the same properties as the preceding.

J. B.

Preparation of Trichloracetic Acid. By A. CLERMONT.*

TRICHLORACETIC acid may easily be obtained pure and in large quantity by the following method:—Hydrate of chloral is put into a flask with three times its weight of fuming nitric acid, and the mixture is left to itself in the sun; a continuous disengagement of hyponitric acid ensues, which ceases at the end of three or four days. On distilling the mixture in a retort furnished with a thermometer, the temperature rises rapidly to 123°, at which point a mixture of nitric acid and water distils over; it then rises gradually to 195°, and the distillate consists of the last portion of the nitric acid, together with a small quantity of trichloracetic acid; the temperature then remains steady at 195°, and the distillation proceeds regularly so long as any acid remains in the retort; the product is a colourless, transparent liquid, which crystallises at 44·8°. In one operation, 300 grams of trichloracetic acid may be produced from 480 grams of hydrate of chloral.

J. B.

Ethyldiacetic Acid and some of its Derivatives. By A. GEUTHER.†

IN preparing the sodium salt of ethyldiacetic acid by the action of sodium on ethyl acetate, the author prefers to employ a large excess of the ether, so that all the sodium may dissolve without any great rise of temperature, which would cause the formation of resinous products, dehydracetic acid, &c.‡

By employing 4 pounds of ethyl acetate to 60 grms. of sodium, the author obtained 165 grms. of the acid, corresponding very nearly with the theoretical amount.§

Action of Phosphorus Pentachloride on Ethyldiacetic Acid.—When the pentachloride (33 parts) is gradually added to ethyldiacetic acid (10 parts), it dissolves without any great evolution of heat, forming a reddish-brown liquid; at the same time large quantities of hydrochloric acid and ethyl chloride are evolved, but no acetyl chloride is formed. The product, which consists of phosphorus oxychloride and the chlorides of several acids, cannot be successfully separated by fractional distillation, and is therefore added gradually to water maintained at a low

* Compt. rend., lxxiii, 112.

† J. pr. Chem. [2], iii, 431—454; and Jenaische Zeitschrift, vi, part 4.

‡ Jenaische Zeitschrift, ii, 397. § Zeitschr. f. Chem., iv, 60.

temperature, when it readily dissolves. On distilling the aqueous solution an oil first passes over with the vapour of water, which does not solidify; this is succeeded by a milky liquid which deposits crystals on cooling, and ultimately the distillate comes over clear. The first portion of the distillate contains a readily volatile oil, which does not solidify; the milky intermediate portion a volatile acid, which solidifies on cooling, and the residue in the retort a very difficultly volatile acid. These three may be more completely separated from one another by repeated fractional distillation with water. The small portion of the volatile acid which accompanies the neutral oil may be removed by agitating it with an excess of a solution of sodium carbonate, and distilling, the crystalline volatile acid being recovered from the sodium salt by distillation with dilute sulphuric acid. In order to obtain the slightly volatile acid from the residue in the retort in the first distillation, it is neutralised with sodium carbonate, and, after separation of the resinous impurities, concentrated by evaporation. Much of the sodium phosphate may thus be separated by crystallisation; and on evaporating the mother-liquors to dryness, and extracting with alcohol, the sodium salt of the new acid is dissolved, leaving the sodium phosphate and sodium chloride. After the alcohol has been removed by distillation, excess of sulphuric acid is added to the solution, and the whole boiled for some time to remove the last traces of the more volatile acid. On agitating with ether, drying the ethereal solution of the acid with calcium chloride, and evaporating, an oil is left behind, which solidifies over concentrated sulphuric acid to a crystalline mass. To purify this acid it is dissolved in water, decolorized by animal charcoal, and recrystallised.

The more volatile acid, which is identical with the monochlorocrotonic acid of Frölich,* the author calls *monochloroquartenylic* acid, from Hofmann's proposed nomenclature for the hydrocarbons;† quartenylic acid ($C_4H_6O_2$) standing in the same relation to quartenyl (C_4H_7) that acetic acid does to ethyl. The chlorinated acid can be boiled with excess of potassium hydrate without undergoing decomposition.

Monochlorotetracrylic acid, $C_4H_5ClO_2$. The difficultly volatile acid from the residue in the retort forms long colourless needles or prismatic monoclinic crystals of high refractive power, melting at 94°, and distilling with partial decomposition between 206° and 211°. The somewhat greasy distillate melts at 89°. The acid is more easily soluble in water than the metameric monochloroquartenylic acid, one part of the acid dissolving in 35·2 of water at 19°, and it is moreover but slightly volatile in the vapour of water. It is a tolerably strong acid, displacing carbonic acid from the carbonates, but is decomposed when boiled with solutions of the caustic alkalis. *Sodium salt*, $2(C_4H_4NaClO_2) + H_2O$.

* Jena. Zeits., v, 82. † Proc. Roy. Soc. xv, 55.

Thin glistening plates, which are very soluble in water and in alcohol. *Barium salt*, $(C_4H_4ClO_2)_2Ba$. Thick, colourless, rhombic octahedrons, soluble in 2·2 parts of water at 18°. *Copper salt*, $(C_4H_4ClO_2)_2Cu + H_2O$. Small blue crystals, obtained by the spontaneous evaporation of a solution of cupric carbonate in the acid. The *silver salt* is a crystalline precipitate, obtained by adding silver nitrate to a solution of the barium salt. *Ethyl monochlorotetracrylate*, $C_4H_4ClO_2,C_2H_5$, is a colourless, highly refractive liquid, of a pleasant aromatic odour, boiling at 184° (corr.), and having a specific gravity of 1·111 at 16·5°. It is prepared by digesting the acid with a saturated alcoholic solution of hydrochloric acid, adding water to separate the ether, and rectifying.

The neutral oil. This is a colourless liquid, heavier than water, which, after being dried by calcium chloride, distilled between 155° and 200° with partial decomposition. The analyses made by the author of the various fractions indicated that it was a mixture of the ethers of monochloroquartenylic acid and monochlorotetracrylic acid. In order to confirm this result, the mixed ethers were decomposed by heating them to 125° for several days in sealed tubes with three times their volume of concentrated hydrochloric acid, opening the tubes at intervals to permit the escape of the ethyl chloride formed. On distilling the product with water, monochloroquartenylic acid came over with the vapour of water, accompanied by a small quantity of an oil boiling between 165° and 195°, which was not further examined. The residue in the retort contained monochlorotetracrylic acid, which was extracted by agitating the solution with ether.

From these results it is apparent that the action of phosphorus pentachloride on ethyldiacetic acid gives rise to the chlorides of monochloroquartenylic acid and monochlorotetracrylic acid, the ethers of these acids, ethyl chloride, hydrochloric acid, phosphorus oxychloride, and a brown resin, probably a secondary product.

$$C_6H_{10}O_3 + 2PCl_5 = C_4H_4ClO.Cl + C_2H_5Cl + HCl + 2POCl_3,$$
$$C_6H_{10}O_3 + PCl_5 = C_4H_4ClO_2.C_2H_5 + HCl + POCl_3.$$

Quartenylic acid, $C_4H_6O_2$. This acid is obtained by treating a saturated solution of sodium monochloroquartenylate with sodium amalgam at the ordinary temperature, adding excess of sulphuric acid, and agitating with ether. After drying the ethereal solution with calcium chloride, and removing the solvent by distillation, the quartenylic acid remains behind as an oil, which may be purified by rectification, 7·5 grms. being obtained from 12 of the chlorinated acid. It is a colourless, oily liquid, having an odour recalling that of butyric acid, and is miscible with water in all proportions. It boils at 171·9° (corr.), does not solidify at −15°, and has a specific gravity of 1·018 at 25°. Its

sodium salt crystallises in deliquescent, very soluble needles; the *barium salt*, $(C_4H_5O_2)_2Ba + 2H_2O$, forms small, permanent, but very soluble crystals; the *calcium salt*, $(C_4H_5O_2)_2Ca + 2H_2O$, very soluble needles or plates. The *lead salt*, $(C_4H_5O_2)_2Pb + H_2O$ consists of colourless interlaced needles, which become opaque when dry, and melt to a semi-transparent mass at 68°. The *silver salt*, $C_4H_5O_2Ag$, is a white caseous precipitate, almost insoluble in water, formed by adding silver nitrate to a solution of the sodium salt. Ferric chloride forms in solutions of the quartenylates, a brownish-yellow, flocculent precipitate; cupric acetate a bright blue precipitate.

Ethyl quartenylate, $C_4H_5O_2.C_2H_5$, is a colourless liquid, of specific gravity 0·927 at 19°, boiling at 136° cor. It has a peculiar, but not unpleasant odour.

The action of fused potash on quartenylic acid was studied by neutralising the acid, evaporating to dryness, and fusing the residue with three times its weight of potassium hydrate until hydrogen ceased to be evolved. When cold, the fused mass was dissolved, acidulated strongly with sulphuric acid, and distilled. The distillate was found to contain only acetic acid and a little unaltered quartenylic acid, so that the reaction may be thus represented: $C_4H_5O_2.K + KHO + H_2O = 2(C_2H_3O_2.K) + 2H$. This decomposition is analogous to that which the metameric tetracrylic acid (solid crotonic acid) undergoes, but differs from that of methacrylic acid, the latter yielding formic acid and propionic acid when fused with potassium hydrate.

Tetracrylic acid, $C_4H_6O_2$ (solid crotonic acid). This acid is obtained from monochlorotetracrylic acid by treating it with sodium amalgam in a manner precisely similar to that previously described for quartenylic acid. The residue left on distilling off the ether solidifies on cooling to a mass of colourless needles which melt at 79·5°. On being purified, however, by crystallisation from water, it resembles the crotonic acid obtained from allyl cyanide, melting at 71·5°, boiling at 187·4° (corr.), and forming thick colourless tables belonging to the monoclinic system. The mother-liquors yield crystals having a somewhat higher melting point, 81° to 81·5°, and containing rather more carbon and less hydrogen than tetracrylic acid. This the author considers to be due to the presence of a small quantity of another acid of higher melting point.

Tetrolic acid, $C_4H_4O_2$, is formed when ethyl monochlorotetracrylate is submitted to the action of potassium hydrate, and may be advantageously prepared from the neutral oily mixture of ethyl monochlorotetracrylate and ethyl monochloroquartenylate by digesting it with a slight excess of potash-solution and a small quantity of alcohol, until the oil entirely disappears. The solution is now boiled to expel the alcohol, supersaturated with sulphuric acid, and distilled as long as

any of the unaltered monochloroquartenylic acid passes over with the water. The acid residue in the retort is then extracted with ether, and dried by calcium chloride, and the solvent is removed by distillation. The brown crystalline residue may be purified by repeated crystallisation from water, when it forms deliquescent, colourless, transparent, rhombic tables, which are readily soluble in water, alcohol, and ether. The dry acid melts at 76·5°, and boils at 203° cor. Tetrolic acid can also be obtained directly from monochlorotetracrylic acid by digesting it with a solution of potash: $C_4H_5ClO_2 = C_4H_4O_2 + HCl$.

Diethyldiacetamide and the Action of Ammonia on Ethylic Ethyldiacetate at a high temperature.—The action of concentrated ammonia on the ether of ethyldiacetic acid at the ordinary temperature, gives rise to two compounds, a soluble amide, $C_6H_{11}NO_2$, the amide of ethyldiacetic acid, and an insoluble amide, $C_8H_{15}NO_2$, which may be regarded either as the amide of diethyldiacetic acid, or as the ethylamide of ethyldiacetic acid. 1. It was observed that the insoluble amide decomposed in presence of moisture, ammonia being liberated and the crystals becoming fluid. The author thought it probable that this decomposition would be more quickly effected by the action of acids. Two grams of the amide were, therefore, agitated with dilute hydrochloric acid, when the crystals rapidly liquefied, and, at the end of a day, the odour of the amide had completely disappeared. On examination, the oily liquid was found to be almost pure ethylic ethyldiacetate, the decomposition taking place in the following manner:—

$$C_8H_{15}NO_2 + H_2O + HCl = C_8H_{14}O_3 + NH_4Cl.$$

This equation requires ·7 grm. of ammonium chloride for 2 grms. of amide: found ·75 grm. From this reaction, it would appear that the insoluble amide is not the ethylamide of ethyldiacetic acid, but the amide of diethyldiacetic acid.

2. Six grams of the insoluble amide were heated to 100° with 27 grams of water in a sealed tube for several days, and afterwards for some time to 130°. The contents of the tube, which had a strong ammoniacal odour, and contained ammonium carbonate, were distilled, and the distillate, after being slightly acidified with sulphuric acid, was re-distilled. The oil (3 grams) came over between 78° and 208°, and consisted chiefly of ethylacetone, together with a little alcohol and some high boiling-point substance. On evaporating the residue in the retort from the first distillation, one gram of the soluble amide of ethyldiacetic acid was obtained. The insoluble amide, therefore, undergoes the decomposition—

$$C_8H_{15}NO_2 + H_2O = C_6H_{11}NO_2 + C_2H_6O,$$

* Jena. Zeitsch., ii, 404.

giving alcohol and the soluble amide, and the latter then further decomposes into ethylacetone, carbonic acid, and ammonia, thus—

$$C_6H_{11}NO_2 + H_2O = C_5H_{10}O + CO_2 + NH_3.$$

The accuracy of the latter equation was proved by heating some of the soluble amide with water to 135°, when it was found to be partially decomposed into ethylacetone and ammonium carbonate.

In order to ascertain the nature of the liquid of high boiling-point, mentioned above, the author heated ethylic ethyldiacetate with four or five times its volume of concentrated ammonia for several days to 100° to 120°. The resulting oil, after being carefully dried, was submitted to fractional distillation, when the first portion, boiling at about 100°, was found to be ethylacetone; that between 190° and 200° unaltered ethylic ethyldiacetate; and the highest fraction, 200° to 215°, gave by analysis, results corresponding with the formula $C_{10}H_{18}O_3$, that of the ethylic diethyldiacetate of Frankland and Duppa*.

From these results it would appear that in the decomposition of ethylic ethyldiacetate by ammonia at a high temperature, and also that of the insoluble amide of diethyldiacetic acid by water, the soluble amide of ethyldiacetic acid is formed, and also a small quantity of ethylic diethyldiacetate, as represented by the following equations:—

$$2C_8H_{14}O_3 + NH_3 = C_{10}H_{18}O_3 + C_6H_{11}NO_2 + H_2O,$$
$$2C_8H_{15}NO_2 + H_2O = C_{10}H_{18}O_3 + C_6H_{11}NO_2 + NH_3.$$

C. E. G.

On Camphoric Acid. By F. Wreden.†

This acid is best prepared by dissolving 150 grams of camphor in 2 litres of nitric acid (sp. gr. 1·27), and heating the solution in a water-bath, till the gases which escape are only slightly coloured. From 1·5 kilograms of camphor 725 to 805 grms. of pure acid were obtained.

C. S.

The Ethers of Arsenic and Arsenious Acids. By J. M. Crafts.‡

Up to the present time the ethers of arsenic and arsenious acids have not been prepared, whereas the combinations of arsenic with alcohol-radicals have long been known. It might seem, therefore, that these ethers are very difficult to prepare. Such, however, is not the case; they are easily obtained by a number of reactions.

Ethyl Arsenate.—This substance is prepared by the action of ethyl

* Ann. Chem. Pharm., cxxxviii, 208. † Deut. Chem. Ges. Ber., iv, 570-571.
‡ J. Pharm. [4], xiii, 242—250.

iodide on thoroughly dried silver arsenate, the two bodies being heated to 100° with ether in a sealed tube. The temperature should not much exceed 100°, and the iodide must not be in excess: otherwise double decompositions takes place between the ethyl arsenate formed and the excess of iodide.

The ethyl arsenate is separated from the silver-salt by washing the product of the reaction with ether, and is purified by distillation under a pressure of 60 mm. of mercury. Under that pressure it boils constantly at 148°—150° (uncorr). It yielded on analysis 31·79 p. c. C., 6·49 H., and 32·85 As., the formula $(C_2H_5)_3AsO_4$, requiring 31·86 C., 6·64 H., and 33·18 As. Its density at 0° is 1·3264, water at 4° being 1; the density at 8·8 is 1·3161.

Ethyl arsenate suffers partial decomposition when distilled in the air, but the greater part passes over undecomposed at 235°—238°. It mixes with all proportions of water, undergoing immediate decomposition into alcohol and arsenic acid. Dry ammonia gas reacts with it to form alcohol and a crystalline body, insoluble in ether, but very soluble in alcohol, the composition of which is not yet perfectly determined.

Methyl Arsenate.—This ether is prepared by the action of methyl iodide on silver arsenate. It cannot be distilled without decomposition at atmospheric pressure; the greater part, however, distils undecomposed at 213°—215°. Under the pressure of 60 mm. it distils at 128°—130°. It gave on analysis 19·90 p. c. C., 4·91 H., and 40·15 As, the formula $(CH_3)_3AsO_4$, requiring 19·57 p. c. C., 4·89 H., and 40·76 As.

The density of methyl arsenate at 14·5° is 1·5591, that of water at 4° being 1. It resembles the ethyl-compound in all its properties.

Amyl Arsenate.—Obtained in the same manner as the preceding compounds, but the author has not been able to obtain it quite pure, on account of its partial decomposition at the boiling-point, even in a vacuum. It undergoes decomposition with water as easily as the other ethers of arsenic acid.

Ethyl Arsenite.—This ether may be obtained by three different processes.

1. When arsenious acid is heated to 200° with silicic ether in a sealed tube, a reaction takes place, which comes to an end in a few hours; a deposit of silica, or of a silicic ether containing so much silica that it is insoluble in ordinary ether, takes place, from which the ethyl arsenite is readily separated in a pure state by distillation.

2. Ethyl iodide reacts with silver arsenite at 150°, yielding ethyl arsenite; but the yield is not so good as in the case of ethyl arsenate. It is remarkable that bibasic silver arsenite yields only the normal ether with three atoms of ethyl.

3. The best reaction for the preparation of ethyl arsenite is that of

sodium ethylate on arsenious chloride or bromide in alcoholic solution:

$$3C_2H_5NaO + AsBr_3 = 3NaBr + (C_2H_5)_3AsO_3.$$

This method of preparation is complicated by a second reaction, which becomes considerable when a certain proportion of ethyl arsenite is formed in the liquid. Sodium alcoholate, in fact, acts as readily upon ethyl arsenite as upon arsenious bromide, according to the equation—

$$(C_2H_5)_3AsO_3 + 3C_2H_5NaO = Na_3AsO_3 + 3(C_2H_5)_2O.$$

For this reason a quantity of sodium ethylate is employed, sufficient to react with three-fourths only of the arsenious bromide, so that at the end of the operation there remains a mixture of the bromide and ethyl arsenite. These liquids are separated by passing into the solution a current of dry gaseous ammonia, which forms with the arsenious bromide a compound insoluble in alcohol and ether, whilst it does not affect the ethyl arsenite. The liquid is then filtered, and the ethyl-compound is obtained pure by distilling off the alcohol or ether with which it is mixed.

Analyses of the body obtained by these various processes have given 34·33 to 34·38 p. c. C., 7·08 to 7·61 H., and 36·34 As., the formula $(C_2H_5)_3AsO_3$ requiring 34·29 p. c. C., 7·14 H., and 35·71 As.

Ethyl arsenite boils without decomposition at 165°—166°, under ordinary pressure. Its density, compared with that of water at 4°, is 1·224. The density of its vapour is 7·615 at 209·5°, 7·608 at 213°, 7·197 at 233°. It is instantly decomposed by water, by the moisture of the air, or by alcohol containing water, giving a deposit of arsenious acid and alcohol. It yields no condensed ether by partial decomposition with aqueous alcohol, as is the case with the silicic ethers.

Ethyl arsenite is not acted on by dry ammonia, and may even be distilled in the gas without alteration. It undergoes with hydrobromic acid a decomposition the reverse of that which usually takes place between haloid acids and ethers, thus:—

$$(C_2H_5)_3AsO_3 + 3HBr = 3C_2H_5HO + AsBr_3.$$

Methyl Arsenite, formed under the same conditions as the ethyl-compound, gives by analysis, 21·67 p. c. C., 5·44 H., and 44·21 As., the formula $(CH_3)_3AsO_3$ requiring 21·44 p. c. C., 5·36 H., and 44·64 As.

It boils without decomposition at 128°—129°. Its density is 1·428, that of water at 4° being 1. The density of its vapour at 197° is 6·006. In its properties it exactly resembles ethyl arsenite.

Amyl Arsenite.—Obtained by the action of sodium amylate on arsenious bromide. It distils under the ordinary pressure at 288°, with

partial decomposition, and under the pressure of 60 mm. at 193°—194°, without decomposition. Analysis showed it to contain 53·01 p. c. C., and 9·72 H., the formula $(C_5H_{11})_3AsO_3$, requiring 53·37 p. c. C., and 9·82 H. It possesses the same properties as the corresponding ethyl- and methyl-compounds, and is easily decomposed by water, the moisture of the atmosphere, or aqueous alcohol.

The author calls attention to the fact that the differences in boiling points due to the substitution of methyl for ethyl in these ethers are those which are not so great as are observed in most ethers of organic acids; and further, that the differences for the ethers of arsenic acid are not the same as for those of arsenious acid.

J. R.

Researches on the Ether-derivatives of the Polyatomic Alcohols and Acids. Part VII, *on the Monochlorides of Diatomic and Bibasic Acids.* By L. HENRY.*

OF the acids $C_nH_{2n}\left\{\begin{matrix}COHO\\COHO\end{matrix}\right.$ only bichlorides are known, but no monochlorides or hydroxyl-chlorides, $C_nH_{2n}\left\{\begin{matrix}COCl\\COHO\end{matrix}\right.$, and there is little hope that such compounds can be obtained, as the chlorine acts upon the hydroxyl, forming the anhydride of the acid and hydrochloric acid. Thus, by acting upon one molecule of succinic acid with one molecule of phosphorus pentachloride, the product of the reaction consists of succinic anhydride.

But these hydroxylchlorides may be replaced by their ether- or alcohol-derivatives, as the oxides of the alcohol-radicals are not acted upon by chlorine.

Ethyloxy-oxalylchloride, $C_2O_2\left\{\begin{matrix}Cl\\OC_2H_5\end{matrix}\right.$, is obtained by acting upon perfectly dry potassium ethyl oxalate with phosphorus oxychloride. It is a colourless mobile liquid with a suffocating smell, having at 16° the specific gravity 1·2160, and boiling at 140°. It fumes strongly in the air, and when exposed to the air for some time, becomes converted into oxalic acid. With water it decomposes very rapidly, and with alcohol it instantaneously forms oxalic ether; with an alcoholic solution of ammonia, it yields ethylic oxamate; and with aniline, ethylic phenyloxamate.

C. S.

On the action of Sodium Amalgam on Oxalic Ether. By A. EGHIS.†

BY reducing oxalic ether with sodium amalgam Friedlander obtained a new acid, $C_2H_4O_4$, which he calls *glycollinic acid.* The author, on

* Deut. Chem. Ges. Ber., iv, 398—601. † Deut. Chem. Ges. Ber., iv, 580—583.

repeating these experiments, found that by this reaction *glycollic acid*, $C_2H_4O_3$, is formed. The pure calcium salt had the composition $C_4H_6CaO_6 + 4H_2O$ and all the properties of calcium glycollate; with calcium chloride it formed the characteristic double salt, $C_4H_6CaO_6 + CaCl_2 + 6H_2O$.* The copper salt had the composition $C_4H_6CuO_6$.

C. S.

On the Gallic Ethers. By F. Ernst and C. Zwenger.†

The ethers of gallic acid, which have hitherto been overlooked on account of their properties being so similar to those of the acid itself, can be readily prepared by passing a current of dry hydrochloric acid through a boiling solution of gallic acid in anhydrous alcohol. When an excess of hydrochloric acid and of alcohol is employed, the acid is almost entirely converted into the ether. On evaporating the dark-coloured liquid to dryness at 100°, slowly heating the residue to its melting point, and then crystallising the product two or three times from water, the ether is obtained in a pure state.

Ethyl Gallate, $C_6H_2\left\{\begin{matrix}(OH)_3\\CO.O(C_2H_5)\end{matrix}\right. + 2\tfrac{1}{2}H_2O$. This ether crystallises from its aqueous solution in transparent rhombic prisms of a pale yellow colour, which melt in their water of crystallisation at 90°. It is without odour, and its solutions have a bitter taste and acid reaction. This ether is only slightly soluble in cold water, but dissolves easily in hot water, and crystallises out almost completely on cooling. It is readily soluble in alcohol and ether, and may be crystallised from chloroform, in which however it is but slightly soluble, in anhydrous colourless needles melting at 150°. When cautiously heated, it sublimes in lustrous needles. Potassium and sodium hydrate decompose the ether in the cold, with liberation of alcohol, and if the air be permitted to have access to the solution, the alkaline gallate formed quickly oxidises, and becomes of a dark colour. The ether gives a precipitate with the salts of most of the heavy metals, but the author did not succeed in obtaining any one of them of a constant composition. The lead salt is a yellowish white precipitate, the zinc salt a white, and the copper salt a reddish brown precipitate. Ferrous salts colour the solution of the ether a pale violet, which changes to blue on exposure to the air, whilst ferric salts give the blue colour at once. Silver and gold salts are quickly reduced in the cold. The only compound of the ether

* The author gives the incorrect formulæ $C_2H_3CaO_3 + 2H_2O$ and $C_2H_3CaO_3 + CaCl_2 + 3H_2O$, although the results of his analyses agree with those for the right formulæ.—C. S.

† Ann. Ch. Pharm., clix, 27—36.

which the author has succeeded in obtaining of constant composition, was prepared by adding a slight excess of a cold saturated solution of acid sodium carbonate to a warm saturated solution of the ether. In a few minutes a compound having the formula $C_7H_4Na(C_2H_5)O_5 + C_7H_5(C_2H_5)O_5$ separated in small hard yellow crystals. These were almost insoluble in cold water, but with care could be crystallised from hot water. The crystals are decomposed by hydrochloric acid, the sodium being removed, leaving pure gallic ether. When they are heated between two watch-glasses, the gallic ether sublimes, whilst the sodium ethylgallate remains behind in a partially decomposed state. On heating a solution of the sodium compound for some time, or still better a solution of the ether in an excess of sodium carbonate, a lemon-yellow crystalline precipitate is obtained, which is insoluble in cold water, but dissolves easily in solutions of the alkaline hydrates; the addition of hydrochloric acid to its alcoholic solution causes a pale yellow crystalline precipitate, which has the properties and composition of ellagic acid, $C_{14}H_6O_8 + 2H_2O$. The lemon-yellow powder is acid sodium ellagate, $C_{14}H_5NaO_8 + H_2O$, and is formed by oxidation of the sodium-compound of ethyl gallate:

$$\left.\begin{matrix} C_7H_4Na(C_2H_5)O_5 \\ C_7H_5(C_2H_5)O_5 \end{matrix}\right\} + O = C_{14}H_5NaO_8 + H_2O + 2C_2H_6O.$$

Acid potassium carbonate has no action on the ether in the cold, but on applying heat potassium ellagate is formed. When a solution of ethyl gallate in ammonia is exposed to the air, it first acquires a rose-red tinge, which after a time becomes deep red, and the solution finally deposits a greenish-yellow crystalline precipitate of ammonium ellagate, which is scarcely soluble in ammonia. This reaction furnishes a good lecture experiment. An attempt to prepare *methyl gallate* from commercial methyl alcohol failed, owing to the latter containing ethyl alcohol, and the crystalline compound obtained from it was found to be ethyl gallate.

Amyl Gallate, $C_6H_2\left\{\begin{matrix}(OH)_3 \\ CO.O(C_5H_{11})\end{matrix}\right.$. This ether crystallises in fine silky colourless needles, which melt at 139° and sublime when cautiously heated. It is without odour and has a bitter taste. It is slightly soluble in cold water, but more readily in hot water, the solution solidifying on cooling to a crystalline pulp. Its solutions have an acid reaction, and when the ether is heated under the surface of water, it melts to an oil. It is readily soluble in cold alcohol and ether, also in hot chloroform. No compound analogous to that obtained from ethyl gallate was observed on treating the ether with acid sodium carbonate, but its other reactions with alkalis and metallic salts were identical with those of the corresponding ethyl compound.

C. E. G.

Synthesis of Oxaluric Acid. By L. HENRY.*

THE author has succeeded in effecting the synthesis of ethylic oxalurate by the action of urea on ethoxyl-oxalyl-chloride:

$$\left\{\begin{matrix}COCl\\COOC_2H_5\end{matrix}\right. + CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right. = \left\{\begin{matrix}CO(CO\left\{\begin{matrix}NH_2\\NH\end{matrix}\right.)\\COOC_2H_5\end{matrix}\right. + HCl.$$

The reaction, which takes place at ordinary temperatures, is extremely energetic and accompanied by considerable evolution of heat. Since the hydrochloric acid formed remains combined with a portion of the urea, it is necessary to employ two equivalents of the latter to one of chloride. The product of the reaction, which forms when cold a hard, crystalline mass, is first treated with water or alcohol, whereby the excess of urea is removed, and then recrystallised from boiling water. Ethylic oxalurate thus obtained forms thin, white, silky needles, which are tasteless and anhydrous; it is very slightly soluble in cold, but much more soluble in hot water; alcohol dissolves it less readily than water; in ether it is almost insoluble; acids, alkalis, and ammonia dissolve it readily. When heated it melts between 160°—170°, but is at the same time decomposed and resolved into oxamethane, or its products of decomposition, and cyanuric acid:

$$\left\{\begin{matrix}CO(CO\left\{\begin{matrix}NH_2\\NH\end{matrix}\right.)'\\COOC_2H_5\end{matrix}\right. = \left\{\begin{matrix}COH_2N\\COOC_2H_5\end{matrix}\right. + CNOH.$$

It is easily decomposed by boiling with water, oxaluric acid probably being formed; the mother-liquors obtained on recrystallising as above exhibit both an acid reaction and acid taste, and the residue obtained on evaporation gave on analysis numbers approximating to those required by oxaluric acid. On heating ethylic oxalurate with alcoholic ammonia for some time at 100° it is converted into oxaluramide.

An attempt to convert oxamethane into ethylic oxalurate by heating with urea to 140°—150° was without result.

The author expects to obtain parabanic acid by the action of ethoxyl-oxalyl-chloride on cyanamide, if this body is really the nitrile corresponding to oxaluric acid:

$$\left\{\begin{matrix}CO(HNCOH_2N)'\\COOH\end{matrix}\right. \qquad \left\{\begin{matrix}CO(HNCN)\\COOH\end{matrix}\right.$$

Oxaluric acid. Parabanic acid.

He further points out that, since alloxanic acid and alloxan bear the same relation to mesoxalic acid as oxaluric and parabanic acids to

* Compt. rend., lxxiii, 195.

oxalic acid, it may be expected that these bodies will be obtained respectively by the action of urea and cyanamide on ethoxyl-mesoxalyl-chloride $\left\{\begin{array}{l}COCl\\CO\\COOC_2H_5.\end{array}\right.$ H. E. A.

Remarks on the Determination of the Relative Positions of the Substituted Radicals in Aromatic Compounds. By H. HUEBNER.*

IN reply to Graebe† the author says that he acknowledges the value of Kekulé's ring formula, but he cannot believe that it gives the real position of the atoms so far as to enable us to anticipate with certainty the results of experiment.

C. S.

Researches on the Constitution of Benzene Derivatives (Second Communication). By V. v. RICHTER.‡

IN the first part of his researches, the author showed that the chloronitro- and bromonitrobenzene from dinitrobenzene, give the metachloro- and metabromobenzoic acids by means of potassium cyanide. He now shows that iodonitrobenzene also yields a meta-acid.

The iodonitrobenzene was obtained from paranitraniline by treating the nitrate of that base with nitrous acid, and decomposing the solution of the azo-compound with hydriodic acid. The dark oil which separated, was distilled in a current of steam; the different portions of distillate, with the exception of the first, readily solidified, and melted at 35°—36°. It was heated with potassium cyanide and alcohol to 200° for three hours, and the resulting liquid boiled with potash, which gave rise to considerable evolution of ammonia. The solution contained meta-iodobenzoic acid, together with a very small quantity of para-iodobenzoic acid. The latter was separated by means of its barium salt; it melted at 267°. In the filtrate from the trifling quantity of barium paraiodobenzoate, the metaiodobenzoate was contained. The meta-acid melted at 155°; it sublimed in fine needles which melted at 156°. The meta-acid was also obtained from anthranilic acid, by passing nitrous acid into aqueous nitrate of anthranilic acid, and treating the solution with hydriodic acid. The iodobenzoic acid thus produced sublimed in fine needles which melted at 157°. By fusing metaiodobenzoic acid with potash, much salicylic acid was obtained; the latter crystallised from water in long needles, melted at 154°, and gave the violet coloration with perchloride of iron. The melting-points of the isomeric iodobenzoic acids are as follows:

* Deut. Chem. Ges. Ber. iv, 611—613. † Page 679 of this volume.
‡ Deut. Chem. Ges. Ber., iv, 553—555.

Ortho (Körner).	Meta.	Para.
172°	157°	267°

The author concludes by giving the melting points of the three bromonitrobenzenes, and shows the connection of some isomeric phenyl derivatives therewith:—

$C_6H_4\left\{\begin{matrix}Br\\NO_2\end{matrix}\right.$ at 125°.	$C_6H_4\left\{\begin{matrix}Br\\NO_2\end{matrix}\right.$ at 56°.	$C_6H_4\left\{\begin{matrix}Br\\NO_2\end{matrix}\right.$ at 37°.
Orthonitrophenol. Quinone. Ortho-oxybenzoic acid.	Dinitrobenzene. Resorcin. Salicylic acid.	Volatile Nitrophenol. Pyrocatechin. Para-oxybenzoic acid.

W. H. D.

Researches on the Constitution of the Twice-substituted Benzenes (Conclusion). By E. ADOR and VICTOR MEYER.*

THE authors, in the present communication, have continued their examination of benzene derivatives in which substitution has twice taken place, *e.g.*, sulphanilic acid, phenolsulphurous acid, bromobenzoic and isophthalic acids, in order to determine to which carbon atoms the substituted elements or groups are attached.

From previous experiments by Meyer or others, *resorcin and terephthalic acid are regarded as belonging to the* 1 : 4 *series*, and *isophthalic acid to the* 1 : 3 *series.*

Sulphanilic Acid.—The formation of terephthalic acid from sulphanilic acid, by the conversion of the latter into bromobenzenesulphurous acid and dicyanbenzene, rendered it possible that sulphanilic acid might belong to the 1 : 4 series.

To confirm this, sulphanilic acid (obtained by means of aniline and sulphuric acid) was converted into bromobenzenesulphonic acid, and the potassium bromobenzenesulphonate was fused with twice its weight of potash. The particular dihydroxylbenzene produced in this case was found to be *resorcin*, and resorcin only, no pyrocatechin or hydroquinone being formed. Now as resorcin and terephthalic acid belong to the 1 : 4 series, sulphanilic acid must be regarded as containing the SO_3H and NH_2 in the places 1 and 4 respectively.

Phenolsulphonic Acid from Sulphanilic Acid.—Sulphanilic acid, treated with nitrous acid, yields a diazo-derivative, $C_6H_4\left\{\begin{matrix}N=N\\ \diagup\\ SO_3\end{matrix}\right.$, which by boiling with water, is converted in phenolsulphonic acid, with evolution of nitrogen. It was thought highly probable that this

* Ann. Ch. Pharm. clix, 1—27.

phenolsulphonic acid would belong to the 1 : 4 series, and, therefore, be identical with Kekulé's paraphenolsulphonic acid. The production of the phenolsulphonic acid from sulphanilic acid is accompanied by the formation of an easily soluble colouring matter, which renders the preparation of the acid for direct comparison a matter of extreme difficulty. Kekulé's acid is converted into resorcin by the action of melting potash; the same was found to be the case with the phenolsulphonic acid from sulphanilic acid; resorcin, free from pyrocatechin and hydroquinone, is formed. The acids from both sources are, therefore, regarded as identical, and as belonging to the 1 : 4 series. Sulphanilic acid warmed with potassium dichromate and sulphuric acid, gave rise to a yellow substance, which resembled quinone in all but its melting point. It melted at 66°; quinone fuses at 115°. It does not appear to have been analysed.

Benzenesulphonic or Phenylsulphurous Acid from Sulphanilic Acid—Schmitt obtained phenylsulphurous acid by heating diazophenylsulphurous acid with absolute alcohol.

$$C_6H_4\left\{\begin{matrix} N{=}N \\ \quad / \\ SO_3 \end{matrix}\right. + C_2H_6O = N_2 + C_2H_4O + C_6H_5SO_3H.$$

This reaction does not take place at the boiling point of alcohol under ordinary pressure; the internal pressure in the vessel in which the decomposition takes place, should be raised by about half an atmosphere. Schmitt regarded the acid thus obtained as isomeric, not identical, with ordinary phenylsulphurous acid. Ador and Meyer found that the acid from sulphanilic acid is rendered difficultly crystallisable by accompanying brown colouring matter, which pertinaciously adheres to the acid and its salts. Owing to its great solubility, the acid is not well adapted for comparative experiments; the following derivatives of the phenylsulphurous acid from sulphanilic acid,—the potassium salt, chloride, amide, and analide, were found to be altogether identical with the corresponding compounds of the ordinary phenylsulphurous acid.

Bromobenzoic and Isophthalic Acids.—The conversion of the former into the latter of these acids, is effected by fusing potassium monobromobenzoate with an equal weight of dry sodium formate. The isophthalic acid and its barium salt were analysed, and recognized by their physical properties. No phthalic or terephthalic acid is produced by the action of the formate, but considerable quantities of benzoic acid are regenerated. This formation of isophthalic acid from bromobenzoic acid gives the latter acid and its analogues a position in the 1 : 3 series.

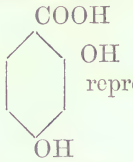
The authors give, at the end of their paper, a very full list of twice-

substituted derivatives of benzene, ranged in columns according to the attachment of the second substituted group or element to the second, third, or fourth carbon atom of benzene. The isomerides are placed in the same horizontal line; in many cases the property by which a specific difference is recognized (*i.e.*, fusing point, product of oxidation), is added.

Their arrangement differs from that of other chemists who have investigated the subject, in placing salicylic acid with its derivatives, chlorosalylic acid, anthranilic acid, &c., in the 1 : 2 (ortho-) series, and oxybenzoic acid, amidobenzoic acid, &c., in the 1 : 3 (meta-) series.

W. H. D.

Preliminary Communication on Dioxybenzoic Acid. By MAX ASCHER.*

THE author confirms Meyer's formula for protocatechuic acid,† 1 : 3 : 4, by showing that the other alternative 1 : 2 : 4, or  represents the constitution, not of protocatechuic acid, but of a new acid. The starting point taken was the sulpho-acid of the 1—4 nitrotoluene, $C_6H_3\left\{\begin{matrix}CH_3\\SO_3H,\\NO_2\end{matrix}\right.$ which Beilstein and Kuhlberg obtained by treating solid nitrotolulene with fuming sulphuric acid; no isomeride is produced at the same time. From this nitrosulpho-acid a dioxybenzoic acid was obtained; but before proceeding to study its constitution, it was necessary to know that of the nitrotoluolsulphurous acid. In this body, the position of the CH_3 to the NO_2 is known, viz., 1 : 4; it was necessary then to find the relation of the SO_3H to the CH_3. To this end, the method used by Meyer was followed: the nitrotoluene-sulphurous acid was converted into amido-acid, this into the azo-derivative, and this last hydrogenised by heating with alcohol under pressure: toluene-sulphurous acid was thus produced.

The toluenesulphurous acid was fused with potash, and the methyl of the liquid cresol thus formed was oxidised into carboxyl by repeated fusion with potash.

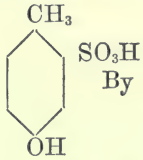
The acid obtained by these operations proved to be salicylic acid; from which it results that, in the sulpho-acid from the solid nitrotoluene,

* Deut. Chem. Ges. Ber., iv, 649—652.

† This is also done by Barth. See page 829.

the position of the CH_3 relative to the SO_3H is 1 : 2, and the constitution of the acid, 1 : 2 : 4.

The nitrotoluenesulphurous acid was then converted into the amido-acid, and this into the diazo-acid. The latter body, on boiling with water, loses nitrogen, and is converted into a cresolsulphurous acid, constituted as follows:—



By fusing the potassium salt of this acid with potash, dioxybenzoic acid is produced, the sulphuric acid residue being exchanged for OH, and the CH_3 being oxidised to COOH. This acid, called by the author 2 : 4 dioxybenzoic acid, has not been completely examined; after drying at 120°, it melts at 194°, and gives with ferric chloride a beautiful reddish-brown coloration.

W. H. D.

On Disulphobenzoic Acid, and on a New Dioxybenzoic Acid. By L. Barth and C. Senhofer.*

By heating benzoic acid with oil of vitriol and phosphoric anhydride in sealed tubes to 250°, the authors obtained disulphobenzoic acid. The contents of the tubes are heated with barium carbonate, and from the solution of its barium salt the disulpho-acid is obtained by treatment with sulphuric acid, and subsequent evaporation. Dried in vacuo, it appears as an exceedingly hygroscopic crystalline mass, which contains water even after heating to 130°, and corresponds to the formula,

$$C_6H_3\left\{\begin{array}{l}COOH\\SHO_3\\SHO_3\end{array}\right. + H_2O.$$

By fusing the potassium disulphobenzoate with caustic potash, a dioxybenzoic acid was produced, which differs from protocatechuic acid in crystalline form, and in giving no coloration with ferric chloride, and no precipitate with lead acetate. The acid melts above 220°. The composition of the air-dried crystals is represented by

$$C_6H_3\left\{\begin{array}{l}COOH\\OH\\OH.\end{array}\right. + 1\tfrac{1}{2}H_2O.$$

It loses the water of crystallisation at 105°. By the dry distillation of dioxybenzoic acid, none of the known dihydroxylbenzenes are produced, but a crystalline yellow body in small quantity, whose composition is not yet determined with certainty. Fusing disulphobenzoic acid with potassium formate, resulted only in the formation of isophthalic acid.

W. H. D.

* Deut. Chem. Ges. Ber., iv, 631; Ann. Ch. Pharm., clix, 217.

On the Preparation of Protocatechuic Acid from Oxybenzoic Acid, and on the Constitution of the former Body. By L. BARTH.*

BARTH, in a previous investigation, showed that protocatechuic acid could be produced from paraoxybenzoic acid as well as from oxybenzoic acid. Remsen showed that the oxybenzoic acid prepared by Barth's process is always accompanied by paraoxybenzoic acid, in consequence of which Fittig doubts whether the source of the protocatechuic acid was not admixed paraoxybenzoic acid.

Barth has again prepared pure oxybenzoic acid, converted it into the sulpho-acid, and decomposed this with potash; by this treatment protocatechuic acid was produced. Sulphoparaoxybenzoic acid also yielded protocatechuic acid; but in addition, a more difficultly soluble acid, which gave a red iron reaction.

If paraoxybenzoic acid is regarded as belonging to the 1 : 4, and oxybenzoic acid to the 1 : 3 series, the position of protocatechuic acid must be 1 : 3 : 4. Fittig regards this arrangement as incorrect, because the dry distillation of protocatechuic acid produces always and solely pyrocatechin. Barth, in regard to this, thinks that the hydroxyls of pyrocatechin may be attached to contiguous carbon-atoms, and that hydroquinone may very possibly have its hydroxyl in the positions 1 : 3.

W. H. D.

On Dimethyl- and Diethylprotocatechuic Acid. By RUDOLF KOELLE.†

DIMETHYLPROTOCATECHUIC acid is prepared by heating 1 gram of protocatechuic acid, 4 grams of methyl iodide, and 1 gram of pure potash, together with some methyl alcohol, in a sealed tube to 140° for some hours. The liquid portion is filtered from the potassium iodide, the alcohol evaporated off, and the oily residue boiled for some time with dilute soda-ley. After cooling, the liquid is acidulated with sulphuric acid, by which means a flocculent deposit of the new acid is produced. This is shaken up with ether, and the insoluble residue repeatedly crystallised from water. It is obtained in glistening, white needles, having the composition $C_6H_3\left\{\begin{matrix}COOH\\OCH_3\\OCH_3\end{matrix}\right.$. It melts at 170°—171°, and does not show the characteristic iron reaction of protocatechuic acid. By distillation with lime, it gives rise to an oil, boiling between 210° and 215°, and having the composition of dimethyl-pyrocatechin:

$$C_6H_4\left\{\begin{matrix}OCH_3\\OCH_3\end{matrix}\right..$$

* Deut. Chem. Ges. Ber., iv, 633; Ann. Ch. Pharm., clix, 230.

† Deut. Chem. Ges. Ber. iv, 634; Ann. Ch. Pharm., clix, 240.

The acid is converted by bromine into *bromodimethyl-protocatechuic acid*, $C_6H_2Br.(OCH_3)_2.COOH$, which crystallises from water in needles.

Diethylprotocatechuic acid, $C_6H_3\left\{\begin{matrix}COOH\\OC_2H_5\\OC_2H_5\end{matrix}\right.$ is prepared in a similar manner to the dimethyl-acid. It melts at 149°, and gives no reaction with iron perchloride. By dry distillation it yields an oil, probably consisting of *diethyl-pyrocatechin*. With bromine it forms a crystalline product, exhibiting the composition of a mixture of mono- and di-bromodiethylpyrocatechuic acid.

W. H. D.

On the Azo-compounds of Resorcin. By P. WESELSKY.*

THE starting point for these compounds, which are all distinguished by their beautiful colours, is *diazo-resorcin*, which is obtained by acting with nitrous acid on an ethereal solution of resorcin—

$$3C_6H_6O_2 + N_2O_3 = C_{18}H_{12}N_2O_6 + 3H_2O.$$

It forms brown granular crystals, with a green metallic lustre; is sparingly soluble in water, dissolves more freely in alcohol and acetic acid, with a dark cherry-red colour, and its alkaline solutions have a splendid blue violet colour. By the action of strong sulphuric or hydrochloric acid it is converted into *diazo-resorufin*, $C_{36}H_{18}N_4O_9$, which separates from the hydrochloric acid solution in small dark red granular crystals. It is nearly insoluble in water, alcohol, and ether; concentrated sulphuric acid dissolves it with a crimson colour, and the same colour is exhibited by its alkaline solutions, which have also a beautiful vermilion red fluorescence. When diazo-resorcin is heated with tin and strong hydrochloric acid, the solution assumes an emerald-green colour, and on cooling, *hydro-diazo-resorufin hydrochloride*, $C_{36}H_{18}N_4O_9.H_{12} + 3HCl$, crystallises out in the form of green leaflets with a silvery lustre, or of light green needles. The crystals, when exposed to the air, assume the colour and the coppery lustre of indigo. On heating this compound in a current of air, the hydrochloric acid escapes, and oxidation takes place, diazo-resorufin being reproduced. When a solution of the hydrochloride is heated with diazo-resorufin, a dark blue solution is obtained, from which dark bottle-green, shining needles crystallise out, which are a combination of the two substances, corresponding to quinhydrone.

By heating diazo-resorcin with acetyl chloride in closed tubes, *dihydro-diazo-resorcin hydrochloride* is formed—

$$C_{18}H_{13}N_2Cl_3O_5 = C_{18}H_{12}N_2O_6 \text{——} H_2O + 3HCl.$$

* Deut. Chem. Ges. Ber., iv, 613—619.

It crystallises in yellow scales, resembling mosaic gold, insoluble in water but soluble in alcohol with a straw colour, and in alkalis with a magnificent violet. By cold nitric acid it is converted into a brick-red flocculent body, which, when treated with warm nitric acid, gives purple plates, the alcoholic or ethereal solution of which shows a really surprising vermilion-red fluorescence. Both compounds are true colouring matters, and the former has the property that the fluorescence of its ammoniacal solution appears also on silk dyed with it. The above reaction of acetyl chloride also gives rise to *acetyl-diazo-resorcin*, in the form of an amber-yellow resin.

By heating diazo-resorcin with concentrated nitric acid, *tetrazo-resorcin nitrate*, $C_{18}H_6N_4O_6.(NO_3)_3$ is obtained—

$$(1)\ C_{18}H_{12}N_2O_6 + N_2O_3 = C_{18}H_6N_4O_6 + 3H_2O.$$
$$(2)\ C_{18}H_6N_4O_6 + 3N_2O_5 = C_{18}H_6N_4O_3.(NO_3)_3 + 3NO_2.$$

It crystallises in well-defined garnet-red needles, having a brilliant metallic lustre, which dissolve in water and alcohol, and very readily in ether with a pure indigo-blue colour. By further action of nitric acid, *tetrazo-resorufin nitrate*, $C_{34}H_6N_8O_9(NO_3)_6$ is formed. The crystals contain water, have the appearance of potassium permanganate, and dissolve with the same colour in water, alcohol, and ether. On drying, the water of crystallisation escapes, and a dull, brick-red powder is left behind. On boiling it with water, decomposition takes place, which is accelerated in presence of alkalis; from the brown solution dark flakes separate out. By the action of nascent hydrogen, it is transformed into *dihydro-tetrazo-resorufin nitrate*, $C_{18}H_6N_4O_6.H_2(NO_3)_3$, which crystallises from its cherry-red alcoholic solution in small needles.

Hydroamido-tetrazo-resorufin hydrochloride, $C_{37}H_{22}N_8O_9.6NH_3.9HCl$, is the final product obtained by heating any of the above tetrazo-compounds with tin and hydrochloric acid. It crystallises in long colourless needles, which, on exposure to the air, assume a rose colour; in alkalis it dissolves with a blue colour. By passing air through the ammoniacal solution, it becomes brown, whilst green crystals, with a cantharide-like reflection separate out. This body is hydro-imido-tetrazo-resorufin, $C_{36}H_{22}N_8O_9(NH)_6$; it is insoluble in water, and dissolves in concentrated hydrochloric and diluted nitric acid, with a wine-red colour.

Mono-nitro-resorcin is contained in considerable quantities in the mother-liquors from the preparation of diazo-resorcin. It crystallises in exceedingly thin and very long straw-coloured needles, which are aggregated in bulbous masses. It forms three series of salts, the colour of which is lemon-yellow, golden-yellow, and dark orange.

C. S.

Two Modifications of Benzophenone. By TH. ZINCKE.*

THE compound $C_{13}H_{10}O$, obtained by oxidising diphenylmethane,† is not an isomeride of benzophenone, but a new modification of this body. It is first obtained as an oily liquid, from which, on standing in the cold, large transparent, apparently monoclinic crystals, separate, which have great resemblance to Iceland spar; they melt at 26°—26·5° to a clear liquid which boils constantly at 300°. The same modification of benzophenone is obtained as a by-product in the preparation of methylphenyl ketone.

After some time the transparent crystals change their appearance; they become milk-white, and this change is accelerated by touching or gently warming them. They melt now at 48°—49°, being transformed into common rhombic benzophenone, which is the more stable form of the two.

C. S.

On Umbelliferone. By H. HLASIWETZ.‡

H. SCHIFF in a recent communication, expresses the constitution of æsculetin by the formula $C_6H_2\left\{\begin{matrix}CH.O\\C.OH\\C.OH\\OH\end{matrix}\right.$, and proves the existence of the alcoholic group C.OH, and of the aldehydic group CH.O, by the formation of triacetyl-æsculetin.

Umbelliferone (a product of the dry distillation of galbanum resin, and of the resins of some umbelliferous plants) shares with æsculetin the property of a bright blue fluorescence of its dilute alkaline solution, and approaches it in composition. Hlasiwetz some years since gave reasons for changing Zwenger and Sommer's formula of umbelliferone ($C_6H_4O_2$) to $C_9H_6O_3$. It thus differs from æsculetin by one atom of oxygen. The author finds that, like æsculetin, umbelliferone yields an acetyl derivative; this it does when heated with chloride of acetyl to 100°; analysis shows, however, that monoacetyl-umbelliferone alone is produced. From this it is concluded that only a single C.OH group is present. The formula of umbelliferone is thus written:—

$$C_6H_2\left\{\begin{matrix}CH.O\\CH.O\\C.OH\\H\end{matrix}\right.$$

Æsculetin heated with potassium hydrate, breaks up into protocate-

* Deut. Chem. Ges. Ber., iv, 576—578. † Journ. Chem. Soc. [2], ix, 508.
‡ Deut. Chem. Ges. Ber., iv, 550—553.

chuic and formic acids; umbelliferone, by boiling with strong potash-ley, yields resorcin, as well as carbonic and formic acids.

$$C_6H_2\left\{\begin{matrix}CH.O\\C.OH\\C.OH\\OH\end{matrix}\right. + 2H_2O + O_2 = C_6H_3\left\{\begin{matrix}COOH\\OH\\OH\end{matrix}\right. + 2C\left\{\begin{matrix}O\\OH\\H\end{matrix}\right.$$

Æsculetin. Protocatechuic acid.

$$C_6H_2\left\{\begin{matrix}CH.O\\CH.O\\C.OH\\OH\end{matrix}\right. + H_2O + O_4 = C_6H_2\left\{\begin{matrix}H\\OH\\OH\\H\end{matrix}\right. + 2CO_2 + C\left\{\begin{matrix}O\\OH\\H\end{matrix}\right.$$

Umbelliferone. Resorcin.

W. H. D.

A New Class of Colouring Matters. By ADOLF BAEYER.*

Gallein and *Gallin.*—Gallein (whose formation by heating pyrogallic acid with phthalic acid and some other substances, has been already described,†) is obtained by crystallisation as a brownish-red powder, or in small metallic-green crystals. It gave on analysis numbers agreeing with the formula $C_{18}H_{14}O_7$; its formation is temporarily represented by—

$$3C_6H_6O_3 - 2H_2O = C_{18}H_{14}O_7.$$

It is not identical with Wackenroder's gallerythronic acid. When gallein is boiled with a large quantity of water to which zinc and dilute sulphuric acid are added, the dark colour of the liquid changes to a light reddish-yellow, and on cooling, oily drops separate, which, after some time, become crystalline. The crystals consist of gallin rendered impure by gallein; the gallin is best purified by crystallisation from a warm aqueous solution of pyrogallic acid. It is obtained in beautiful glistening rhombohedrons and prisms, which are nearly colourless; dried *in vacuo*, they yield, on analysis, numbers which give for gallin the composition $C_{18}H_{16}O_6$. Gallin, in the solid state, or in aqueous solution, very readily assumes a red colour; it is less stable than hæmatoxylin, which in other respects it greatly resembles. It dyes mordanted fabrics like gallein.

Cærulein and *Cærulin.*—When gallein is heated with 20 pts. concentrated sulphuric acid to 200°, the reddish-brown colour of the liquid changes to greenish-brown. The heating is continued until a portion of the liquid, when warmed with water, deposits dark flakes, but does not give a coloured solution; the mass is then poured into a large quantity of water, and the bulky blackish precipitate is washed

* Deut. Chem. Ges. Ber., iv, 555—558. † Page 699 of this volume.

with hot water. This precipitate is pure cœrulein; dried at 180°, its composition is expressed by the formula $C_{18}H_{10}O_6$; its formation from gallein by—

$$C_{18}H_{14}O_7 - H_2O - H_2 = C_{18}H_{10}O_6.$$

Cœrulein is but slightly soluble in water, alcohol, or ether; it dissolves easily in hot aniline, with a magnificent blue colour; such a solution, slightly acidulated with acetic acid, dyes wool an indigo-blue tint. Fabrics mordanted with alumina are dyed green; those mordanted with oxide of iron are dyed brown by cœrulein; the colours bear soaping well, and rival madder colours in stability.

By reducing agents cœrulein is converted into cœrulin, a substance which dissolves in ether with a yellow colour; the ethereal solution shows a beautiful green fluorescence. The cœrulein is most easily reduced by ammonia and zinc dust. The Chinese possess a green dyestuff, of vegetable origin, called Lo-Kao, which appears to be very similar to cœrulein.

Fluorescein and *Fluorescin.*—By heating together phthalic anhydride and resorcin, Baeyer has obtained a body which he calls fluorescein, on account of the magnificent green fluorescence which its solution in ammonia exhibits. Fluorescein dyes silk and wool a fine yellow, without the use of a mordant. By the action of zinc dust and ammonia it is converted into fluorescin. These two bodies do not appear to have yet been analysed.

W. H. D.

On the Primary and Secondary Phosphine of the Methyl Series. By A. W. Hofmann.*

These compounds are formed in the same way as the corresponding ethyl compounds,† by heating in closed tubes, 2 mol. phosphonium iodide, 2 mol. methyl iodide, and 1 mol. zinc oxide. A solid crystalline mass is thereby obtained, from which the phosphines are isolated by a method similar to that used for the preparation of the ethyl compounds. The methyl-phosphine, which escapes as a gas on adding water to the product of the reaction, is condensed in a flask surrounded by a mixture of ice and calcium chloride. The residue in the flask, which towards the end of the operation has to be heated in order to drive out all the monophosphine, solidifies on cooling to a mass of large, beautiful, perfectly white needles, a compound of dimethyl-phosphonium iodide with zinc iodide, from which the base is liberated by adding a solution of caustic soda; it is condensed in a vessel surrounded by ice water.

* Deut. Chem. Ges. Ber., iv, 605—611. † Page 713 of this volume.

Methylphosphine, CH_3PH_2, is a colourless transparent gas, having even a more overpowering smell than ethylphosphine. By cold or pressure it may be condensed into a liquid lighter than water, which boils at $-14°$. It is insoluble in water, sparingly soluble in ether, more freely in alcohol. In contact with air it fumes, being gradually oxidised, but takes fire when gently heated or when brought in contact with chlorine, bromine, or nitric acid. With acids it forms well-defined salts, which are all decomposed by water, and have the remarkable property of bleaching vegetable colours like chlorine. On holding in the gas a strip of litmus-paper partially moistened with water and partly with an acid, only the latter portion is bleached, showing that the free base itself has not this property.

The *hydrochloride*, $CH_3PH_2.ClH$, is obtained by mixing equal volumes of hydrochloric acid gas and methylphosphine; both gases disappear completely, the salt condensing in well-defined four-sided plates. It is so volatile that it evaporates with ether-vapour. Its solution in concentrated hydrochloric acid gives with platinum chloride a double salt forming orange-red crystals. The *hydriodide*, CH_3PH_2IH, is obtained in thick crystals, by passing the gas into highly-concentrated hydriodic acid. By passing the gas into concentrated sulphuric acid, it is absorbed without blackening of the liquid, and set free again on addition of water. The sulphite is an amorphous white mass, obtained by mixing sulphurous acid and methylphosphine over mercury. Carbonic acid and hydrogen sulphide do not act upon it, but it combines with sulphur, carbon bisulphide, and chlorocarbonic ether.

Dimethylphosphine, $(CH_3)_2PH$, is a colourless liquid, lighter than water, and insoluble therein. It boils at 25°, or at the same temperature as its isomeride, ethylphosphine, $C_2H_5PH_2$. It takes fire at once in contact with air, burning with a bright phosphorus flame. Its salts are all very soluble; the hydrochloride forms with platinum chloride a well-crystallised double salt. It also combines with sulphur and carbon bisulphide.

C. S.

On the Constitution of Rosaniline. By H. BAUMHAUER. (Deut. chem. Ges. Ber. iv, 547.)

Practical Observations concerning Mustard Oil. By F. A. FLÜCKIGER.*

CONCENTRATED sulphuric acid, which gives characteristic colours with most oils, mixes completely with mustard oil without producing a sensible change of that kind.

If three parts of oil of vitriol be added drop by drop to mustard oil,

* Arch. Pharm., cxlv, 214—220.

both being cooled by ice, decomposition sets in, with evolution of sulphurous acid, which may be identified by passing the evolved gas into water. Oxysulphide of carbon, CSO, is evolved at the same time, or rather continues to be evolved from the cooled mixture for twelve hours, and can be detected by passing the vapours through a tube containing fragments of soda, and subsequently testing for the sulphide which results from the reaction—

$$COS + 4NaHO = Na_2CO_3 + Na_2\dot{S} + 2H_2O.$$

Free hydric sulphocyanate does not seem to be produced by the action of oil of vitriol on mustard oil, for neither before nor after the reaction does the mixture give a red reaction with ferric chloride. If the mixture be left without warming, it sets into a mass of crystals, smelling of sulphurous acid, but free from the odour of mustard oil.

In the testing of the commercial oil, note must be taken of the possible presence of cyanide of allyl. As pure sulphocyanate of allyl has a sp. gr. of 1·01, while that of the cyanide is only 0·838, the density of the oil will afford some insight with regard to this point. The boiling point should also be observed. If mustard oil be heated to 50° with one part alcohol and three to four of the strongest aqueous ammonia, the whole of the sulphocyanate will be converted into thiosinammine, part of which will crystallise out on cooling, leaving the rest in solution to be recovered by evaporation of the liquid. The thiosinammine must be white, and the mother-ley should leave either no residue, or only a trifling one, of allyl cyanide.

C. H. G.

Fermentation of Fruit. By G. LECHARTIER and F. BELLAMY.*

FRUIT protected from the air evolves considerable quantities of carbonic acid. At the same time alcohol and acetic acid are formed in the interior of the fruit, whilst a proportional diminution takes place in the quantity of sugar it contains.

The facts cited below have been observed with apples, but the authors are satisfied that they are equally true of currants and cherries.

The following are the results of some experiments :—

* J. Pharm. [4], xiii, 251—254.

	Duration of expt.	Weight of apples.	Loss of weight.	Loss of sugar.	Gas evolved.	Alcohol.	Acetic acid.
1..	184	348·0	14·3	26·0	13·10	10·01	0·11
2..	157	353·6	7·6	6·0	5·30	4·00	0·10
3..	234	531·5	22·5	36·4	21·05	20·56	0·29
4..	150	407·3	31·3	45·6	24·50	21·80	0·35
5..	124	338·9	3·9	5·4	3·00	2·89	0·17
6..	184	341·0	4·0	..	2·40	4·27	0·17

In the later stages of the evolution of carbonic acid, the authors invariably found the alcoholic ferment fully developed and budding at all parts of the interior of apples, the peel of which remained intact. In the juice of apples the globules became transformed into long chains in the course of a few hours. During the first stage of evolution of gas, however, no ferment in the growing state was found either in the apples or in the juice expressed from them. The juice contained only isolated globules of various sizes; but even at this stage, alcohol was formed, as shown by experiment 5. The authors have not observed the ferment in the budding state in apples exposed to the air. The question, whether in this case alcohol is formed in the fruit, remains to be decided by experiment.

The gas evolved from the interior of an apple under reduced pressure was found to contain 15 p. c. of oxygen, and 5 of carbonic acid, the rest being nitrogen. The gas evolved from mellow or rotten apples contains no oxygen.

J. R.

Physiological Chemistry.

Fundamental Difference between the structure of Albumin and that of Casein. By J. A. Wanklyn.*

In ultimate percentage composition albumin and casein are indistinguishable; in oxidation-products they have, up to the present time, been regarded as alike. Only in some small reactional characters, as, for instance, that the one is, and the other is not, precipitable by acetic acid, had they been distinguished. They differ, however, remarkably in the quantities of ammonia which they yield by oxidation with an alkaline solution of potassium permanganate, casein, as shown by the author, yielding only 6·5 p. c. ammonia, whereas albumin yields 10 p. c. This difference in the yields of ammonia

* Pharm. J. Trans. [2] ii, 66; from the Milk Journal.

points to deep-seated difference in chemical structure, and shows that albumin and casein, which are metameric, and possibly even isomeric with one another, belong to different chemical families.

Inasmuch as the albuminous compounds of young mammals have necessarily been obtained by metamorphoses of the casein supplied in the milk which they feed upon, the process of assimilation must consist partly in fundamental chemical change, and not merely in morphological changes and superficial chemical alterations.

Researches on Animal Starch. By C. DARESTE.*

SEVERAL years ago M. Dareste pointed out the existence of granules having the physical and chemical characters of starch in the yolk of the hen's egg. In the newly-laid egg these characters are often masked by the presence of albuminous, oily, and other matters, from which the granules are freed with difficulty. He now finds that they can be easily demonstrated in eggs, during that stage of incubation when the yolk-sac has become completely separated from the intestine of the embryo chick, by simply placing a few drops of the fluid from the yolk-sac under the microscope. It is then seen to contain granules, which are about ·025 mm. in diameter, and when examined by polarised light, present the optical characters of starch. Unlike those in the newly-laid egg, they do not always give a blue with iodine, not unfrequently becoming red. Similar observations have been made by Nægali, on vegetable starch which has become partially absorbed, and Dareste thinks that the starch-grains in the egg are absorbed and disappear, and that the increase in the amount of glucose found by Lehmann during incubation is due to their transformation. Three, or perhaps four successive series of granules appear in the ovum. The first are found on the inner surface of its external membrane, while it is still in the ovary. The second are those found in the yolk before incubation. The third occur in the mucous layer of the blastoderm, and the formation of the *area pellucida* is partly due to their disappearance. Later on, when the intestine and yolk-bag have become separate, they are found in the vitelline appendices. The fourth are produced in the liver, and form its glycogenic matter. The successive appearance and disappearance of starch may be due, he thinks, to the transformation of starch into glucose, and its re-formation from glucose. T. L. B.

Note on the Constitution of Milk and Blood. By M. DUMAS.†

IN reference to artificial substitutes for milk, M. Dumas thinks that besides albumin, fat, and salts, it may contain minute quantities of other

* Compt. rend., lxxii, 845—848. † Arch. Sci. phys. nat. [2], xli, 105—119.

substances difficult to recognise, and yet important for nutrition. In an artificial substitute these would probably be omitted, and the nutrition of children or others fed upon it would consequently suffer. In illustration of this he refers to the observation of Raulin, that *Aspergillus niger*, a small fungus growing on citrons, cannot be cultivated successfully in a soil composed of definite chemical compounds, unless a trace of zinc oxide be present. He finds that the formation of lactic acid during churning does not increase the amount or quicken the production of butter, and that the addition of bicarbonate of soda to the milk previous to churning has no other action than slightly to increase the amount of butter. He still holds the view, now abandoned by most physiologists, that blood consists, like milk, of small vesicles swimming about in a fluid, and supposes that scurvy and alcoholism are due to alterations in the osmosis of the corpuscles from diminution of potash and increase of soda-salts in the serum in the former, and the presence of alcohol in it in the latter case.

T. L. B.

Action of Carbonic Oxide on Blood Globules. By CLAUDE BERNARD.*

REFERENCE is first made to the well known fact that carbonic oxide gas exerts a special toxic action on the red blood-globules, and that it communicates a peculiar hue to these, which is different from that produced by oxygen; that the poisoned globules are no longer capable of taking up oxygen; and that Chenot's explanation of these phenomena by the assumption that the carbonic oxide exerts a reducing action, being itself converted into carbon dioxide, is untenable. The following physiological explanation is advanced by M. Bernard:—If we suppose a blood-globule in the lungs to be in presence of an atmosphere contaminated with carbonic oxide, a minute quantity, even a trace, of this gas suffices to produce toxic phenomena. The red globule finding itself in presence of oxygen and of carbonic oxide, can absorb either one or the other; but since its avidity for carbonic oxide is much greater than for oxygen, it absorbs that gas in preference to this, and the oxide cannot be expelled by oxygen. Here, then, is a case of chemical displacement precisely similar to the expulsion of carbonic acid from a carbonate by sulphuric acid. To prove this, M. Bernard puts some arterial blood, oxygenated, and still warm, beneath a bell-jar, then passes in pure carbonic oxide, and agitates. On leaving it to stand for some time, no change of volume is observed, but the gas is now found to be a mixture of carbonic oxide and oxygen. CO has replaced O in the globules, volume for volume. Hence M. Bernard was led to employ carbonic oxide for the analysis of the gases of blood.

* J. Pharm. [4], xiii, 255—266.

The author, in order to account for the *killing* of the red globules, supposes that these are veritable organisms, each living its own life in the plasma of the blood; but that they also form part of an organism to the life of which they are indispensable. Among the albuminous substances which compose the globules, *hæmoglobin*, the colouring matter of blood, is the most important, and the one which plays the chief function in the physiological phenomena accomplished by the corpuscles. This function is entirely chemical, for the oxygen absorbed by the globules forms a true, although feeble, combination with the hæmoglobin. Now hæmoglobin has a great affinity for carbonic oxide, and forms with it a true chemical compound, more stable than the corresponding oxygen-compound, so that this latter is decomposed by carbonic oxide. This new chemical compound readily crystallises.

Having thus removed the phenomena of carbonic oxide poisoning from the region of "vital" phenomena into that of chemical physics, and shown that they consist in the formation of a stable compound of hæmoglobin and carbonic oxide, and consequent inertia or insusceptibility of change in the globules, M. Bernard has endeavoured to ascertain whether it is possible to recognise with certainty asphyxia by the vapours of burning charcoal. Troja had already noticed, in the last century, that the blood of animals thus asphyxiated is sometimes florid, and we now know that this is due to the formation of CO–Hb.* But the peculiarity of this form of blood is that it retains its florid colour when submitted to the action of carbonic anhydride, and CO–HB is sufficiently stable to resist for a considerable time the influence of decomposition. Bernard has further shown that carbonic oxide may be resorted to as an agent for preserving blood, and a process has been proposed for the preservation of meat, founded on these observations.

When normal blood is heated in a tube, it speedily blackens, whilst the poisoned blood retains its red colour; the former is blackened by potash or soda, whilst the latter is unchanged by the alkalis. These properties, which are referable to CO–Hb, are met with in the blood of animals poisoned by carbonic oxide, even long after death; it is possible to exhibit them in blood taken from putrefied corpses, or with blood that has been long dried. CO–Hb may, however, be detected in much more minute quantities by its spectroscopic peculiarities. CO blood exhibits, when thus examined, two dark absorption-bands in the yellow, very difficult to distinguish from those of oxygenated blood. The two bands of CO blood persist when the blood is treated with such reducing agents as reduced metallic iron or ammonium sulphydrate, and the single-banded spectrum of reduced hæmoglobin is not obtained by this

* The symbol CO–Hb is frequently employed in continental literature to indicate the compound of hæmoglobin with carbonic oxide; O–Hb to indicate oxy-hæmoglobin, &c.—T. S.

means. It cannot be affirmed, nevertheless, that these spectroscopic peculiarities may not be brought about by other substances. A perfect demonstration of carbonic oxide poisoning requires the extraction of the gas from the blood, and the verification of its reactions; this has been achieved by Gréhant, who has disengaged the carbonic oxide from its combination with hæmoglobin by means of sulphuric acid at a slightly elevated temperature, and then collected the gas by means of the air-pump. This experiment requires many precautions, and a comparative experiment should always be made at the same time with normal blood.

By examining spectroscopically from time to time the blood of a rabbit that had been exposed to an atmosphere charged with carbonic oxide, Bernard was able to determine the period required for the elimination of the poison from the blood, and on the same principle he states that the best means of detecting the gas in the air of an apartment is that of examining the blood of an animal which has been kept in it.

Although it has been surmised that carbonic oxide is eliminated from the animal body in the form of carbonic anhydride, Bernard is of opinion that the gas is excreted unchanged as carbonic oxide. This hypothesis is, however, not supported by any experiments. As a toxic agent, carbonic oxide acts simply by preventing absorption of oxygen by the red corpuscles of the blood.

For the analysis of the gases of blood by carbonic oxide, Bernard combines the actions of a mercurial pump and of the gas. The blood is introduced into a glass globe communicating with the pump, in which a vacuum has been previously made, and the vessel is then placed on a sand-bath, in order to facilitate the disengagement of the gases. The blood is drawn for analysis from a vein or artery, as the case may be, by means of a graduated syringe, into which a volume of carbonic oxide equal to that of the blood required has been previously introduced. Access of air is thus prevented, as also the production of carbonic anhydride. The blood withdrawn is agitated, in order to facilitate the combination of the carbonic oxide with the hæmoglobin, and then introduced into the globe in which a vacuum has been previously made. The rest of the operation is reduced to a simple gas analysis.

In 100 volumes of blood he found of oxygen:—

	Arterial blood.	Venous blood.
1. Renal secretion very active. Strong dog ..	17·44	16·
Blood in right heart	—	6·44
2. Active renal secretion	19·46	17·26
Suspended renal secretion. Strong dog	—	6·40
3. Medium active secretion	12·	10·
4. Secretion almost inactive. Weak dog.....	5·69	6·45

In an experiment made by Bernard, arterial blood, on its entrance into the muscle of the thigh of a dog, was found to contain 7·31 per cent. by volume of oxygen, whilst the venous blood of the same muscle contained only 5 volumes of this gas; 2·31 volumes appeared to have disappeared in the muscle.

T. S.

Behaviour of Albuminous Matters and Ferments with Phenol. By Dr. N. Zapolsky.*

These experiments show that solutions of albuminoïds are precipitated by phenol only when this substance is in concentrated solution (nearly saturated in water), and when the reaction of the solution of albumin is neither very acid nor perceptibly alkaline. With more dilute solutions of phenol, turbidity of solutions of egg-albumin was obtained, but this was probably due, not to the albumin present, but to the traces of globulin-substances always present in egg-albumin; and so, perhaps, are all the precipitates obtained to be referred to globulin substances. Since the precipitates obtained with these substances are insoluble in dilute solutions of sodium chloride, but soluble in dilute hydrochloric acid and in sodium carbonate, it would appear that the reaction is dependent on a change of the globulin-substance into syntonin, a change which can be effected by the action of any weak acid. Phenol also acts upon this body like an acid, but is unable to dissolve acidalbumin. Since albuminous substances which are soluble in water are completely changed by very dilute and feeble acids into syntonin, it may be supposed that they all undergo the same alteration under the action of phenol. Experiments have, however, not been made by the author in this direction.

In experimenting upon ferments with phenol it was found that the formation of oil of mustard, the formation of hydrocyanic acid from bitter almonds, the conversion of the starch in flour into sugar by diastase, and the change of starch into sugar by saliva, were in no degree prevented by phenol. The solution of fibrin by pepsin at a temperature of 37° was, however, impeded or prevented by phenol according to the quantity of that substance present.

Yeast-cells were found to become contracted and deformed when submitted to the influence of phenol, and it was also found that a solution of this substance extracts more solid material from yeast than does distilled water. These changes probably have some connection with the cause of the action of phenol upon alcoholic fermentation.

T. S.

* Med.-chem. Unters., 1871, 557—560.

Putrefactive Processes and Disinfection. By F. HOPPE-SEYLER.*

THIS paper takes up the subject of the preceding memoir by Zapolsky, that observer having been unable to extend his investigations to putrefactive processes and the vital actions of the lowest organisms.

The altered views of Liebig on fermentation, putrefaction, and eremecausis, are first detailed, and then Pasteur's statements relative to the necessity of living organisms for the commencement and carrying on of fermentation and putrefaction. The author asserts that he has repeatedly observed milk become sour, and curdle, as quickly when kept in hermetically-sealed tubes with exclusion of air, as when the tubes were loosely closed. Hence the ferment must be in the milk itself.

Such ferments as Zapolsky experimented with are separable in the pure state, so that here at least organisms are not indispensable to the fermentative changes. Organisms are necessary for the new formation of ferments, but for fermentations themselves only when the ferment cannot be separated without decomposition. If, in a fermenting solution exposed to the air, we find numerous organisms of definite form, and these grow and multiply in the solution as fermentation advances, we may conclude that the solution contains everything necessary for the development of the organisms. If we find further that the introduction of these organisms into a non-fermenting liquid capable of fermentation, sets up a definite process of fermentation, it is indubitable that these organisms contain a ferment that induces the fermentation in question. It is not, however, thus proved that such a fermentation cannot begin without the concurrence of organisms, and, further, that fermentation may not go on after the death of these, provided the ferment contained in them survives the death of the organism without decomposition, and continues to act under conditions which render impossible the life of the organism as a whole. Experiments were undertaken in support of this view; the author thinks they show that Pasteur's opinions are untenable, and prove the necessity of separating the ferment and its processes from the life and growth of the lower organisms.

Besides less important processes of putrefaction, Hoppe-Seyler enumerates the following:—1. The metamorphosis of albuminous matters into peptone, leucine, tyrosine, butyric acid, hydrogen sulphide, ammonia, and carbon dioxide. 2. The hydration of urea into carbonic acid and ammonia, of hippuric acid into glycocine and benzoic acid. 3. The conversion of lactic acid into butyric acid, carbon dioxide, and hydrogen; the analogous fermentation of malic acid; the decomposition of gluten, with formation of CO_2 and H_2; and, lastly, the generation

* Med.-chem. Unters., 1871, 561—581.

of CO_2 and CH_4 in the mud of marshes and in the large intestine of animals.

A filtered, quite transparent, but highly fluorescent portion of the serum of pus was sealed up in a glass-tube with a small quantity of air directly after filtration, and kept for about six years at the ordinary temperature of a room. In this time the fluorescence had completely disappeared, and a precipitate had formed entirely composed of spherules, which to the naked eye appeared to be composed of silky needles. On opening the tube there was a trifling escape of gas containing some carbon dioxide and a trace of hydrogen sulphide. The crystals consisted of tyrosine; no trace of organisms could be detected, and in the clear solution, together with butyric acid and crystalline fatty acids soluble in water, there was found only a very small quantity of the previously abundant albuminous matter precipitable by boiling and acidification; but, on the other hand, much leucine, tyrosine, and peptonoïdal bodies.

Further: filtered, entirely transparent, fresh hydrocele fluid was sealed up in a glass tube with a small quantity of air, and kept for 32 days at a temperature of 35° to 45°. The fluid quickly became turbid and deposited a flocculent precipitate which, as well as the solution itself, acquired a yellowish-green colour, and at first increased in quantity, then appeared to decrease. On opening the tube, carbon dioxide escaped in abundance with a very perceptible admixture of hydrogen sulphide; traces of hydrogen were also found in the gases given off. So much gas was absorbed by the liquid, that on pouring it out on a filter, there was a lively effervescence. The odour of these gases was exactly that of putrid pus. Microscopical examination of the flocky-granular precipitate quickly separated by filtration, showed absolutely no trace of organisms. Analysis of the fresh and of the decomposed solutions respectively, showed that the loss of organic substances through putrefaction was 5·283 grams per litre, but that this loss was not entirely due to carbon dioxide and hydrogen sulphide, since butyric acid and ammonia were lost by evaporation, so that the actual loss was somewhat less than that stated above. The saponified fats had disappeared, and cholesterin, to a great extent, so that it would appear that this body is not a product of the splitting up of albuminous bodies, nor yet of their hydration, but is formed by oxidation like the fatty acids. The alcoholic extract yielded leucine and tyrosine, and a further quantity of these was found in the aqueous extract, amounting to 7·1 per 1000, so that the yield of leucine and tyrosine was in the aggregate over 10 per 1000. Peptone bodies, precipitable by lead acetate and ammonia, were found in the watery extract. These were not accurately identified. Lecithine was probably present both before and after putrefaction. Butyric acid, mixed with some

valeric and caproic or caprylic acid, had been formed during putrefaction to the extent of 1·388 grams per litre.

Whilst the fluid sealed up and heated to 40° had undergone so much change in composition that only traces of coagulable albumin remained, another portion of hydrocele-fluid which had remained loosely corked at the ordinary temperature for the same period, and swarmed with monads and vibriones, still contained much albumin. Its quantitative determination was abandoned, on account of difficulties in filtration and consequent loss of water and volatile matters. Nevertheless, the putrefaction of albumin had advanced further in an equal length of time in the portion of fluid heated to 40°, in spite of the absence of organisms, than in the portion filled with organisms at 12° to 20°.

Hydrocele-fluid sealed up in glass tubes with a minimum of air, and kept for three months at ordinary temperatures, underwent very slight putrefactive changes compared with that kept in similar tubes at 40°; nevertheless, butyric acid and hydrogen sulphide were formed. It results from these experiments that the greater rapidity of putrefaction at higher than at lower temperatures, does not result from an increase in the number and rapidity of development of living organisms, but on the direct influence of temperature upon the putrefactive process itself.

As regards the influence of phenol on putrefactive changes, it was found that when phenol was added to mixtures of yeast and hydrocele-fluid, not only could the development of the organisms be prevented, but also the action of the ferment on albumin; but that whilst 0·5 per cent. of the crystallised phenol sufficed for the destruction of the organisms, the decomposition of albumin proceeded, although slowly, when as much as 1 p. c. of phenol had been added. Commencing coagulation of the albumin appears to set a limit to the splitting up of that substance by water and a ferment.

Recently, of all putrefactive changes, the formation of carbon dioxide and ammonia from urea has been especially regarded as being dependent on the action of minute organisms; but the author's experiments show that this is not the case, for the graduated addition of phenol kills the organisms before stopping the hydration of urea. The action of the acid on ferments is analogous to that of heat. If a solution containing a ferment be heated, the organisms first perish as the temperature rises, then the ferment becomes altered. The graduated addition of phenol effects the same results. The alcoholic fermentation is exceptional, for in this case the death of the organism and the cessation of fermentation occur simultaneously when the solution is heated to 54°, or when it is treated with a sufficiency of phenol.

The ferment which converts lactates into carbonic and butyric acids appears to be destroyed by a temperature ever lower than that which

prevents putrefactive changes: a temperature of 58° was found to be sufficient for this.

Whilst it is proved with regard to some fermentative processes, and asserted for others, that living organisms are unnecessary to their commencement, it is not asserted that these processes do not stand in a determinate relation to the life of the lower organisms. A small quantity of a ferment is capable of fermenting a large quantity of a fermentable substance, but there is a limit to this. A ferment cannot renew itself. An organism is necessary for the formation of a new portion of ferment, and generally the fermentation, formation of new ferment, and development of organisms proceed *pari passu*. There is thus seen to be a connection between the formation of a ferment and certain organisms though we are not justified in assuming that a definite ferment is exclusively the product of a definite species of plant or animal. Without doubt the lower organisms make use of the ferment to set up fermentation, and thereby sustain their nutrition and activity, just as we derive support from the ferments produced by the minute organisms of which we ourselves consist. It has indeed been asked, what advantage can the yeast-plant derive from the formation of carbon dioxide and alcohol? The gain cannot well be here a material one, for the substances which serve for the growth of the cells must originate from other sources; since then the process is associated with the growth and increase of the cells, the influence can only be a gain of force.

When a ferment acts upon another chemical substance, it cannot well be otherwise than that this substance enters into a combination, however loose, with the ferment, and that this compound then splits up in such a manner that the products of fermentation are formed and the ferment is regenerated. A determinate consumption of energy is necessary to this chemical movement, which must be derived either from the heat belonging to the liquid which undergoes fermentation, or from the forces present in the fermentable matter. In the first case there would be cooling of the liquid during fermentation, and if gases are given off the heat necessary for the expansion of these would be less than the loss of heat which the solution undergoes. If, on the other hand, the necessary force for the chemical movements is derived from the energy set free by the splitting up of bodies during the fermentation, there may be increase of temperature, more heat being set free than is requisite for that work. It is well known that this latter occurs during the splitting up of sugar into alcohol and carbon dioxide. Accurate observations on other kinds of fermentation are wanting from which to draw a definite conclusion. Theoretical considerations induced Hoppe-Seyler to conclude that, during the conversion of starch into dextrin by the pancreatic juice, increase of temperature must occur, and this was verified experimentally. In most processes of

fermentation with which the lower organisms are associated, direct experiment is scarcely possible so as to secure positive conclusions as to the usual alterations; but since these processes go on only at sufficiently elevated temperatures, the author thinks it can scarcely be doubted that in all these fermentations heat is set free, and that a large class of the lowest organisms live by these processes, deriving their forces, not like green plants, from the solar light and warmth, nor like animals from their affinity for oxygen, but from the relatively smaller forces set free during the splitting up of complex organic bodies into more simple substances. *Pari passu* with these changes the lower organisms develop in fermenting solutions. Fermentations are possible without organisms, but definite organisms with a definite life are not possible without definite fermentations.

It is inconceivable that all the higher organisms, plants and animals, should not derive advantage from the fermentations going on in them, and indeed we are entitled to accept this supposition; for the contractions of our muscles, the movements of the protoplasm of our lymph-cells, as well as of those of the lowest organisms, receive the impulse which splits them up, not from the oxidation of organic bodies, but from a fermentative process, and that the products of this splitting up then for the first time readily fall under the influence of oxidation in case oxygen has access to them.

Speculations are next entered into respecting the moot question whether such organisms as cysticerci, echinococci, trichinæ, &c., live without oxygen. Perhaps they, like the yeast plant, require oxygen merely for fructification.

After reference to Pettenkofer's well-known views as to cholera-germs, the author asserts that although deodorants, as ferrous sulphate, destroy the ill-smelling products of fermentation, it must not be supposed that the infective material of such diseases as cholera and typhus is thereby necessarily destroyed, and that in disinfecting we must not rest contented with merely destroying bad smells. He is of opinion that metallic salts act as disinfectants chiefly by precipitating ferments, and along with these the lower organisms. He has proved that $\frac{1}{20}$th of green vitriol suffices to prevent all development of infusorial life in a solution; but it is questionable whether the ferment and the organisms are respectively so changed and destroyed as to be incapable of showing their activity renewed under altered conditions. Phenol has of late been largely used in disinfection; Hoppe-Seyler's researches show that the destruction of organisms is admirably achieved by the use of a very small quantity of this agent, but that the prevention of fermentation demands the use of a much larger amount of the phenol. 1 per cent. of this reagent will effectually put an end to organised life, but 2 per cent. is required to put a stop to putrefactive changes.

Sulphurous oxide gas appears to him to be the most effective agent for destroying germs in the air. 14·3 to 28·6 grams of sulphur burnt for each cubic metre of space to be disinfected entirely prevents the growth of fungi. These quantities of sulphur give 1 and 2 vol. per cent. of sulphurous oxide gas respectively.

T. S.

Physiologico-chemical Notices. By F. HOPPE-SEYLER.*

1. NOTE *on Urinary Calculi.*—Hoppe-Seyler examined a group of three stones of a dirty-white colour and curious shape, which had been removed from the bladder of an elderly man after death. Two of these were 7 c.c. in diameter, meniscus-shaped, and laid against each other so as to form a sort of box, in which lay the third stone, which was smooth, flat, and elliptical. The form of the stones seemed to indicate that the middle one was the remnant of an old calculus which had become partly dissolved while the other two were growing. This, however, does not seem to have been the case, for, in that case, some difference in the composition of the third stone from that of the other two might be expected, whereas, with the exception of a somewhat larger content of calcium salts, it was the same. All three were composed of ammonio-magnesium phosphate, calcium phosphate, calcium carbonate, magnesium carbonate, and insoluble organic matter. Uric and oxalic acids were absent. The cause of their peculiar form still remains doubtful. The existence of hollows in the interior of many urinary calculi may possibly be explained by the deposition of crystalline material round a nucleus of organic matter, which becomes afterwards dissolved. The fissures in other calculi generally filled with a material having the same composition as the rest of the stone, though occasionally different, may be due to the substance of the stone not only being deposited on the outside, but filling the interstices and by crystallising in them, causing tension and cracking.

A calculus which the author examined was greyish-green outside and reddish within, and consisted in both parts, notwithstanding the difference of colours, almost entirely of xanthine, 97 per cent. being found in the outer, and over 98 per cent. in the inner layers. No trace of uric acid, hypoxanthine, guanine, cystine, oxalate of lime, &c., was found.

2. *Guanine in the Urine of the Heron* (*Ardea cinerea*).—Hoppe-Seyler sought in vain for guanine in the excrement of fowls and geese, but E. Haerter has succeeded in obtaining it in his laboratory from the excrement of a heron which was fed partly on fish and partly on flesh.

3. *On the Urine of Pseudopus serpentinus.*—The dried urine could be

* Med. Chem. Untersuch., 1871, 582—587.

easily separated from the fœcal part of the excrement. From 5·781 grms. were obtained 4·3617 grms. uric acid, ·0015 grm. Ca, and ·0348 grm. K., ·0162 grm. alkaline chlorides, and ·441 grm. sand. Scarcely a trace of ammonia and no sodium was found. A trace of urea seemed to be present. The bases are insufficient to saturate the uric acid, and it is, therefore, contained chiefly in the free state in the urine of Pseudopus and also in that of Lacerta viridis. The excretion of uric acid in the urine of this animal is much like that which Meissner found in that of birds. Hoppe-Seyler thinks that urea and uric acid are formed in the kidney and not, as Meissner believes, in the liver.

4. *On the Occurrence of Gelatigenous Tissues in Invertebrata.*—Chondrin was found in the cartilaginous parts of cephalopods by Valenciennes, and by Froriep in Hoppe's laboratory, in snails and mussels; but true gelatin had not been discovered in Invertebrata till Hoppe obtained it in considerable quantities by boiling, from the flesh of *Octopus and Sepiolas.* As Froriep sought for it in vain in cockchafers, vineyard snails, Anadonta and Unio, it would seems that the cephalopods are more closely allied to the vertebrata in this respect than other invertebrate animals.

5. *The Production of Pyrocatechin from Carbo-hydrates.*—A concentrated solution of grape-sugar is heated with a sufficient amount of caustic potash in a water-bath, protected as much as possible from air, and neutralised with sulphuric or hydrochloric acid. It is then shaken with ether, which takes up a substance giving the reactions of pyrocatechin mixed with brown resinous substances. The ether is distilled off, the residue dissolved in water, and filtered. The filtrate gives a green colour with chloride or oxidised sulphate of iron, and a brown with alkalis. It reduces alkaline solutions of cupric oxide slowly on standing, but quickly when heated. It reduces neutral solutions of silver nitrate almost instantaneously at ordinary temperatures. It agrees with pyrocatechin also in its smell and in subliming in currents of carbonic acid gas. It is difficult to purify. Together with it formic, ethylidene-lactic, and carbonic acids are also produced.

Pyrocatechin, with formic and carbonic acids, is also produced by the action of water in sealed tubes on Swedish filter-paper, starch, cane-sugar, and milk-sugar. No such substances were produced by the action of boiling dilute sulphuric acid.

From this behaviour of carbohydrates to water at a high temperature, and to alkalies at a lower one, it is very probable that they are decomposed in this way in the animal body, and especially that cellulose is thus dissolved in the intestines of herbivora, perhaps by the assistance of ferments. It is not improbable that it is associated with the formation of hippuric acid in them.

T. L. B.

Agricultural Chemistry.

Experiments on the Transpiration of Watery Fluid by Leaves. By W. R. M'NAB.*

THE experiments were made on the cherry-laurel, *Cerasus Laurocerasus*. The leaves were found to contain 63·4 per cent. of water. Of this quantity about $\frac{1}{10}$ is transpirable in the sun, in dry air, or *in vacuo*, without injury to the plant; the remainder of the fluid exists as cell-sap. Small branches of laurel, supplied with water at the cut end, exhaled the following amounts of fluid under the various conditions described:—

Condition of Branch.	Fluid transpired per 100 of Branch.
In dry atmosphere, sunshine	20·52 per hour.
In saturated atmosphere, sunshine	25·96 ,,
In dry atmosphere, shade	1·69 ,,
In saturated atmosphere, shade	None ,,
In atmospheric air, sunshine	7·50 per hour.
In oxygen, sunshine	12·77 ,,
In nitrogen, sunshine	1·97 ,,
In carbonic acid, sunshine	4·01 ,,
Both sides of leaves coated with collodion, sunshine	·96 per hour.
Under side of leaves coated, sunshine	1·34 ,,
Upper side of leaves coated, sunshine	12·33 ,,
Both sides of leaves coated, shade	2·56 per 48 hours.
Under side of leaves coated, shade	2·82 ,,
Upper side of leaves coated, shade	16·08 ,,

The high rate of transpiration in the first two experiments was obtained in warm weather and very bright sunshine.

The author determined the rapidity with which fluid ascends the plant during transpiration, by placing the cut end of the stem in a solution of lithium citrate (a method suggested by Mr. Church), and then ascertaining, by incineration and by observation with the spectroscope, the height which the lithium had reached in a given time. In an experiment with a branch of five leaves placed in the sun, lithium was found in 30 minutes at the extreme point, a distance of $9\frac{4}{12}$ inches. On another day lithium was found at a height of $4\frac{9}{12}$ inches in ten minutes. The rapidity of ascent is in proportion to the rate of transpiration, and must diminish as the fluid rises.

R. W.

* Journal of Botany, ix, 19.

On the Distribution of Potash and Soda in Plants. By E. PELIGOT.*

BOTH soda and potash have hitherto been regarded as essential constituents of plant-food. The author had, on the contrary, maintained in previous papers that soda was absent in many cultivated plants, although in other plants growing under the same conditions, soda is always present. The quantities of soda shown in published analyses were determined by indirect methods, the actual presence of soda never having been ascertained. Cloëz and Payen disputed the author's conclusions, and regarded soda, at least under certain circumstances, as a true plant-food for the crops excepted by the author. They showed that crops grown near the sea always contain soda in considerable quantity, and that the "suint" of sheep fed on hay so grown also contains soda.

The author replies that all plants growing near the sea have on their surface more or less of salt deposited from the air, and that the fleeces of sheep are necessarily subject to the same deposit. M. de Gasparin examined wheat grown near the sea in a soil rich in soda. The soil contained 1·64 per cent. soda, and ·205 per cent. potash. The wheat-grain yielded ·071 per cent. soda, and ·379 per cent. potash. The author washed a sample of wheat from this locality with cold distilled water; the solution contained much sodium chloride. By germinating the wheat in water, still more sodium chloride was removed in solution. Samples of various crops grown in the Bay of Bourgneuf yielded to washing, soluble salts, of which 50 to 85 per cent. was sodium chloride.

Potatoes appeared to the author to be suitable subjects for experiment, being protected from the atmosphere during growth. He failed to detect soda in the ash of 1 kilogram of potatoes grown at Bourgneuf. His method is to remove, by crystallisation, the greater part of the potassium as nitrate, convert the residual alkalies into neutral sulphates, and crystallise. Soda is indicated by the efflorescence of the sulphates, and is estimated by calculation from a determination of sulphuric acid in the weighed sulphates. Dehérain failed to detect soda in potatoes manured with soda salts. The author also failed to detect soda in colza seed.

The author concludes that many plants contain no soda; that others, as beetroot, the *Atriplex hortensis*, and *Tetragonia expansa*, always contain it; and that all plants grown near the sea contain chloride of sodium mechanically held.

Payen observes on this paper that soda is always lost in incineration if the charred mass is not exhausted with water before completing the calcination. Washing the plant will also probably remove soluble

* J. Pharm. [4], xiii, 225—238.

salts contained in the outer cells. He refers in illustration to the presence of alkaline oxalates of potassium and sodium in the surface glands of *Mesembryanthemum cristallinum*, and to the presence of crystallised calcium carbonate in the leaves of *Urticaceæ*, and in the stones of the fruit of *Celtis;* in the latter instance the carbonate forms 60 per cent. of the tissue. Champion found soda unmistakably in potatoes which had undergone a second growth, "pommes de terre mères."

R. W.

Researches upon the Existence and Action of Nitrous Acid in Soil. By CHABRIER.*

THE author has determined the proportion of nitrous and of nitric acid in various cultivated and uncultivated soils. The amount of soil operated on was 1 kilogram; it was exhausted by the process employed in the nitre factories of Algeria. For the methods of analysis the author refers to the *Comptes rendus* lxvii, 1031, and lxviii, 63. The results are shown in the following tables, in which the figures represent milligrams per kilogram:—

I.—*Cultivated Soils from Saint-Chamas, Bouches-du-Rhône.*

No.	Character of Soil.	Moisture at 110°.	Nitrous acid.	Nitric acid.
1..	Corn land, surface, in dry weather, winter....	49500	1·17	75·94
2..	The same, taken from a depth of 25 centimetres	121100	3·15	55·52
3..	Olive field, surface, in dry weather, winter ..	30400	·73	22·58
4..	The same, taken from a depth of 25 centimetres	88000	1·98	13·19
5..	Vineyard, taken in dry weather, winter.....	33000	·86	16·28
6..	Plantation of almonds, in dry weather, winter	46000	1·57	13·32
7..	Kitchen garden, taken in dry weather, winter.	22000	4·52	46·29
8..	The same, taken during irrigation, summer ..	155000	·95	11·05

II.—*Uncultivated Soils.*

9..	"Terre d'un Coussou,"† dry weather, spring.	12000	·07	127·90
10..	Pine forest, taken in dry weather, winter	36000	·92	33·97
11..	Pine forest among rocks, dry weather, winter.	23000	·57	11·75
12..	Indurated clay from old river bed, autumn ..	16000	None.	49·00

Samples 1 to 6 were taken on the same day. It appears that all the cultivated soils examined contained nitrous acid. The garden soil stands first in this respect, then the corn land, and lastly the soil

* Compt. rend., lxxiii, 186—191. † Uncultivated land on the chalk.

growing fruit trees. Nitrates were, in dry weather, much more abundant in the surface soil than at the depth of 25 centimetres; while nitrites were on the contrary far more abundant in the lower soil than at the surface. When brought to the surface by capillary attraction, nitrites are most probably converted into nitrates. The uncultivated soils contained very little nitrous acid; this was the case even with No. 9, a soil rich in nitrates, and yielding excellent crops when cultivated. The author proposes further researches on the subject.

R. W.

On the Absorption of Gases by Soils. By F. SCHEERMESSER.*

HYDRATED ferric oxide has a great power of retaining carbonic acid. The amount of carbonic acid held by soil increases with the proportion of ferric oxide present. Pure clay and sand have hardly any power of retaining carbonic acid. The carbonic acid of soils is readily lost in sunshine, but regained in the shade. There is always more present in the morning than in the evening. Hydrated ferric oxide, in presence of water, decomposes calcium carbonate in a very marked manner.

R. W.

Chemical Researches on Beetroot, Part V. *The Distribution of Mineral Substances in the Root.* By B. CORENWINDER.†

THE author has examined samples of Italian beetroot from Modena, Milan, Bologna, and Vicenza, and compared their composition with that of French beetroot from the departments of Nord and Pas-de-Calais. The Italian beets were poor in sugar and contained much saline matter. 1 litre of juice yielded 52·5 to 85 grms. of sugar, and 10·2 to 16·2 grms. of mineral salts. The juice of the French beets gave 90·7 to 132·4 grms. of sugar, and 7·3 to 8·7 grms. of salts per litre. The density of the juice from the Italian beets was comparatively high. Density is not a safe indication of saccharine value, owing to the disturbing influence of the saline ingredients. The amount of potash in the Italian beets was very considerable. Taking all the samples into account, it appears that the proportion of potash bore an inverse relation to the amount of sugar. Some of the samples of Italian beet contained a large proportion of chlorides; in these cases the proportion of soda was also excessive. The following analyses show, however, that sodium is taken up by the plant in other forms beside that of chloride. The analyses were made on three samples of French beet

* Chem. Centr., 1871, 462.

† Compt. rend., lxxiii, 95—99.

grown in the same field with different manures; the quantities refer to 1 litre of juice.

	No manure.	Chemical manure.	Earth-nut cake.
	grm.	grm.	grm.
Chloride of sodium	1·238	·798	1·611
Potash	2·308	2·327	2·315
Soda	·902	1·125	·699
Lime	·216	·160	·371
Magnesia	·322	·293	·231
Sulphuric acid	·406	·201	·182
Phosphoric acid	·581	·657	·444
	5·973	5·561	5·853

The chemical manure consisted of superphosphate, nitrate of potassium, and nitrate of sodium.

The author draws particular attention to the fact, that the juices from these differently manured roots each contained the same quantity of potash and soda.

R. W.

Results of Manures applied to Beetroots. By O. Cech. (Dingl. Polyt. J. cc. 499.)

Analysis of a so-called Universal Manure. By H. Vohl. (Dingl. Polyt. J. cc. 497.)

Analytical Chemistry.

Estimation of Free Hydrofluoric Acid. By P. Guyot.*

As the well-known method of Rose for the estimation of hydrofluoric acid is undoubtedly somewhat complex, and liable to error from multiplicity of operations, it is proposed to replace it by a volumetric process, based upon the reaction, that an alkaline fluoride gives with ferric chloride a precipitate of sesquifluoferrate of the alkali, in virtue of the equation—

$$Fe_2Cl_6 + 10KFl = Fe_2Fl_6.4KFl + 6KCl.$$

* Comptes rendus, lxxiii, 273.

The hydrofluoric acid, if in the free state, is exactly neutralised with potassium carbonate, and then titrated with a standard solution of ferric chloride, in a manner described by the author in a previous communication. It is stated that the reaction proceeds uniformly in presence of potassium sulphate, nitrate, or chloride, but that it is preferable to employ potassium carbonate rather than sodium carbonate, for the neutralisation of the acid, since the precipitate produced by the former salt is much less soluble in water.

J. W.

A New Method of Incinerating Animal and Vegetable Substances: its Application in the Estimation of the Mineral Constituents of Yeast. By A. Béchamp.*

It not unfrequently happens that considerable difficulty arises in effecting conveniently, and without loss, the incineration of animal and vegetable substances. This is especially the case when some of the mineral constituents are volatile, or when the ashes so obtained are fusible; and many and various remedies have been devised to overcome these obstacles, such as the addition of spongy platinum, the carbonates of barium and sodium, peroxide of iron, &c.; the author, however, objects to the employment of these substances, on the ground that in the first place their practical utility is but questionable, and further that their use violates one of the principal laws of chemical analysis, inasmuch as it is improper to employ as reagent, a salt which cannot be readily eliminated, or which may possibly already exist as a natural constituent of the object analysed.

After considerable experience, he recommends the employment of bismuth oxide, in the form of a standard solution of the nitrate as a reagent fulfilling all the conditions required. It is sufficiently infusible, furnishes a certain quantity of oxygen, is never met with in organized bodies, and can be easily eliminated by a volatile reagent incapable of acting upon the products of combustion; and, finally, it forms with sulphuric and phosphoric acids, and with chlorine, combinations sufficiently stable to resist the moderate degree of heat at which the incineration takes place. The combustion is made in the following manner:—

The material, in a finely divided state, is impregnated with a known volume of the bismuth solution, carefully dried and burnt. The ash is then treated with nitric acid, or, if there is no objection, with dilute

* Comptes rendus, lxxiii, 337—341.

hydrochloric acid, in which, if the operation has been successfully conducted, the whole should dissolve. The cold solution is decomposed with sulphuretted hydrogen, and the bismuth sulphide having been filtered off, the liquid is submitted to analysis. When the ash contains phosphates, it may be exhausted with very dilute nitric acid, in which, as is well known, bismuth phosphate is insoluble.

The author continues his experiments upon the composition of beer-yeast, employing the above-mentioned process for the estimation of its mineral constituents. The yeast having been purified by washing with distilled water, and by filtration, was rendered as homogeneous as possible, and a weighed quantity was dried at 100° C. to ascertain its degree of hydration; a second portion was then taken, the proper quantity of bismuth solution added, and the combustion effected in the manner already described. The ash was moistened with a little nitric acid, and heated a second time before weighing, lest it should chance to contain any reduced bismuth. The tabulated results of two analyses, compared with similar analyses by Mitscherlich, are as follow :—

			Analyses by Mitscherlich.	
	I.	II.	Superior yeast.	Inferior yeast.
Sulphuric acid, SO_3 ..	6·376	5·046	—	—
Phosphoric acid, PO_5 ..	63·866	53·443	53·730	34·13
Potash	28·791	31·521	39·500	40·80
Soda	1·929	0·771	—	0·50
Lime	2·491	2·395	1·020	1·15
Magnesia	6·546	3·772	6·150	7·32
Ferric oxide	7·342	2·734	—	—
Alumina	—	traces.	—	—
Silica	traces.	traces.	—	16·60
	100·000	99·682	100·400	100·50
Percentage of ash in dry yeast	7·669	9·730	7·65	?

Particular attention is directed to the presence of sulphuric acid in these analyses, which acid certainly did not exist as an impurity in the yeast, as the latter was washed with distilled water until the wash-waters were free from sulphuric and phosphoric acids.

To determine the extent to which the inorganic constituents were capable of being removed by boiling water, 140 grams of yeast in paste, representing 30·8 grms. of material dried at 100° C., were boiled with 400 c.c. of water for some time, then filtered, the liquor evaporated, and the residue dried at 100°. The latter weighed 7·61 grams. Both were separately incinerated.

Ash of the insoluble portion	0·490
Do. soluble ,, ...	2·246
	2·736

It will be observed that more than three-fourths of the mineral portion of the yeast is taken up by boiling water, the proportion of the soluble constituents, *inter se*, being practically in the same ratio as previously existed in the unboiled yeast.

J. W.

On the Use of a Reflector in Spectrum Analysis. By H. FLECK.*

INSTEAD of using the source of light in front of the collimating telescope, the author places a concave mirror there, so that the prism of the spectroscope is at the focus of the mirror; the source of light is placed at a short distance from the observing telescope, and is thus under the command of the observer; the mirror is so arranged that the light is reflected along the axis of the collimator, and that a second source of light (for a comparison spectrum) can also be reflected on to the small prism in front of the slit. In this way a much stronger illumination is obtained, besides greater facility in observation. From experimenting upon the calcium spectrum, the author believes that calcium is not a simple substance, but a group of nearly allied chemical bodies. A solution of pure calcium chloride which had been standing in contact with calcium sulphate to free it from any possible traces of strontium or barium, was separated into five portions by fractioning with ammonic oxalate. The first and last precipitates gave different spectra. The first gave the red, green, and blue lines sharply defined, and the spectrum from the last precipitate contained red and yellow green bands. The blue line also in the extreme violet disappeared in the third fraction of calcic oxalate, and did not again appear in either the fourth or fifth fractions. In this way the author believes he has separated ordinary calcium compounds into several elementary substances.

A. P.

On the Application of Molecular Rotation to the Determination of the Value of Cinchona Barks. By E. J. DE VRIJ.†

OF the five known cinchona alkaloïds, two, namely, quinine and cinchonidine, deflects the plane of polarization to the left (lævogyre, ↖) the other three, quinidine, cinchonine, and the amorphous alkaloid,

* J. pr. Chem. [2], iii, 352—355. † Pharm. J. Trans. [2], ii, 1.

deflect it to the right (dextrogyre, ↗). Two of them, viz., quinine and the amorphous alkaloïd, are very soluble in ether; the other three are sparingly soluble.

To apply these properties to the valuation of cinchona barks, the total amount of alkaloïds in a bark was determined; the alkaloïds dissolved in weak acetic acid, were decolorised by precipitating lead sulphide in the solution, then precipitated by sodic hydrate, washed, and dried; a weighed quantity was dissolved in a definite volume of dilute sulphuric acid; and the rotating power of the solution determined. The solution may prove inactive, or it may rotate the plane to the right or to the left, according to the proportionate quantities of the alkaloïds present.

The molecular rotation of the mixed alkaloïds may be calculated by the following formula:—

$$[a]j = \frac{a^\circ\ V}{p} \text{ ↖ or ↗.}$$

in which a = the amount of rotation found, right or left handed, as the case may be, p = weight of alkaloïds, and V = volume of solution (and in a tube 100 mm. long). Another portion of the alkaloids is then treated with ether, and the rotatory power of the part insoluble in ether is determined in a similar way.

Two data are thus obtained, which the author believes will prove of great utility in the investigation of cinchona barks. A number of determinations are appended of cinchona barks from various sources, which differ very considerably in their rotating power. The instrument used in these researches is the polaristrobometer of Wild.

A. P.

The Optical Analysis of Bees-wax. By H. Pocklington. (Pharm. J. Trans. [2], ii, 81.)

Examination of Flour. By H. Ludwig. (Arch. Pharm. [2] cxlvii, 1—27.)

On the Determination of Available Chlorine in Bleaching Powder. Remarks on Mr. Herreshoff's Paper on the same Subject (*p.* 751.) By G. Lunge. (Chem. News. xxiv, 5.)

Technical Chemistry.

Mallet's Process for the Preparation of Oxygen. By J. PHILLIPS.*

MALLET'S process depends on the power of cuprous chloride to absorb atmospheric oxygen, and to give it off again when heated to about 400°. The cuprous chloride is best prepared by heating cupric chloride rather strongly, whereby one half of the chlorine is evolved, and can be utilised in preparing more cupric chloride. The cuprous chloride, when moistened and exposed to air, absorbs oxygen, with formation of oxychloride of copper, *e.g.* :—

$$Cu_2Cl_2 + H_2O + O = CuCl_2.CuO + H_2O.$$

The resulting mass, when again heated, first gives off water, and then the oxygen, leaving cuprous chloride. This taking up and giving off of oxygen may be repeated as often as desired; 50 kilos. of cupric chloride, when treated in this fashion, will give 1·5 cubic metres of oxygen at each operation. The apparatus employed in working this process on a large scale, is described in the original paper.

C. H. G.

Silvering of Glass. By KRIPPENDORF.†

THE paper contains practical directions, by following which non-chemists may succeed in silvering glass plates. The reagents required are:—1. Sodio-potassic tartrate. 2. A two per cent. solution of this salt. 3. Caustic ammonia. 4. Solution of silver nitrate, 1 : 8 (old silver-bath will serve). From these, the silvering and reducing liquids are prepared.

1. *The reducing liquid.*—Take 900 c.c. distilled water, and 90 c.c. of the solution of the tartrate; mix and boil strongly, and while the steam is issuing violently from the flask, drop in 20 c.c. of the silver solution, and boil for yet other ten minutes. This solution not only keeps, but seems even to improve by age. The liquid must be filtered from precipitated silver as it is wanted.

2. *The silvering solution.*—Take 900 c.c. distilled water, add 80 c.c. of the silver solution, and 100 drops of the ammonia solution. Filter if necessary.

The silvering process.—Equal volumes of the two solutions are carefully and separately filtered, and poured together into a flat glass dish to such a depth that the carefully cleaned plate, when immersed, shall be covered by a layer at least 2—3 mm. deep.

* Dingl. polyt. J., cc, 466—469. † Dingl. polyt. J., cc, 484—487.

Decomposition of the mixture takes place in ten minutes, and pure metallic silver is deposited on the plate, which has then to be washed, dried, and varnished. For the purpose of silvering the interior of glass globes, &c., it is sufficient to pour in successive small quantities of the mixture, keeping the vessel turning so as to maintain the whole surface wet.

C. H. G.

Cobalt Ultramarine. By W. STEIN.*

THE author has previously shown (p. 166) that blue body-colours result from the *intimate* admixture of black and white molecules, which, when only mechanically mixed, produce grey. In the mechanical mixture producing grey, black and white are seen together, while in the molecular mixture, black is seen through white. As another example of this molecular mixture standing between the mechanical and the atomic, he chooses cobalt ultramarine, which, he shows, by direct experiment, to consist of alumina (or aluminic silicate) mixed with a black cobalt oxide, of the composition expressed by $4CoO.Co_2O_3$.

C. H. G.

Phosphorus Bronze. By MONTEFIORI-LEVY and KIMTZEL.†

THE authors have again drawn attention to the fact that copper alloys containing phosphorus are distinguished by great hardness and tenacity.

The editor of Dingler's Journal gives a number of valuable references to papers and patents relating to the same subject.

C. H. G.

Use of Neutral Water-glass for Wool Washing. By BAERLE & Co., Worms.‡

TAKE one part of neutral water-glass to 40 parts water at 40—45° R., lay the wool in this for a few minutes, and work it a little with the hand, then rinse out with cold or lukewarm water. In this way a wool is obtained quite white, and thoroughly scentless; it remains very soft, and suffers no harm unless it be allowed to remain in the solution for several days, and is then washed out with hot water.

The same solution may be employed with advantage in washing sheep, or for ordinary household work.

C. H. G.

* J. pr. Chem. [2], iii, 428—431. † Dingl. polyt. J., cc, 379—383.
‡ Dingl. polyt. J., cc, 423.

A New Brilliant Green for Wool. By C. PFUNDHELLER.*

To 20 pounds of goods (cloth, flannel, or yarn) take ½ lb. *red* prussiate of potash and 1 lb. English sulphuric acid; put these with the goods† into a cold vat of woad, and heat rapidly to boiling with steam. Keep the whole boiling for an hour, lift out the goods, and add to the boiling liquor 1½ oz. picric acid (more for a yellow shade, less for a blue one); put the goods back and boil for another quarter of an hour, when they will be finished.

The green so prepared resembles the so-called Saxony green, but is much finer. It is absolutely necessary to put the goods and the above reagents together in the *cold*, and to heat rapidly to the boiling point.

C. H. G.

Preparation of Vegetable Parchment. By COLIN CAMPBELL.‡

THE ordinary method of dipping unsized paper in diluted sulphuric acid, gives satisfactory results only when the greatest care is observed with regard to the strength of the acid and the duration of the operation. In Campbell's method the paper is first dipped in a strong solution of alum, then, after being well dried, it is drawn through concentrated sulphuric acid. The alum prevents too strong an action of the acid on the paper, which has only to be washed and dried slowly. The discoverer of this process proposes to make parchment in endless lengths, by putting the alum and sulphuric acid bath in connection with the paper-making machine. Paper which is already printed on can be converted into parchment by this plan.

C. H. G.

The Extraction of Aniline Colours. By DR. REIMAN.§

THE bleaching of goods dyed with aniline colours can only be effected by chlorine when they consist wholly of cotton. When wool or silk is also present, some process of reduction must be employed. Dr. Reiman advises that a solution of stannous chloride (tin salt) of about 1°—2° B. be used, or when this proves ineffective, that a very weak bath of potassium cyanide (½°—1° B.) be employed. The greater part of the paper is devoted to a description of the details which must be observed in using the latter solution, in order to avoid danger to the workmen.

C. H. G.

* Dingl. polyt. J., cc, 423.

† There is no mention of the volume of water to be used.—C. H. G.

‡ Dingl, polyt. J., cc, 506.

§ Dingl. polyt. J., cci, 61—64.

On Transparent Aniline Lacquers, and on a Method for Colouring Mica. By FERD. SPRINGMÜHL.*

THE author prepares alcoholic solutions of various resins, and adds to them solutions of a suitable aniline salt possessing the requisite tinctorial power. He employs for the most part bleached shellac, to which he adds, if desirable, other resins, and dissolves in spirits containing 90—95 per cent. of real alcohol, by allowing the powdered resins to digest at a gentle heat in close vessels for about 24 hours, before filtering through asbestos. Dilute solutions are concentrated on a water-bath. Sandarac added in small quantity increases the elasticity and durability of the lacquer, and oil of turpentine its lustre. Other resins are sometimes added, according as they suit the colours. A concentrated alcoholic solution of the colour is prepared separately, and added to the lacquer just before it is used. The objects to be covered with coloured lacquers should be bright and clear, and not too thick. Mica is treated in its settings, and, like glass, previously heated to about 30° C., to cause it to receive an uniform lacquer.

Aniline-violet is dissolved in the strongest alcohol; a few drops of acetic acid are added, and the whole gently heated with the alcoholic solution of the resin, so as not to produce any turbidity. The intensely coloured solution of the lacquer is then placed on the warm glass or mica, and is left to dry in a warm place (20° to 25° C.) till a clear and smooth, but intensely coloured coating, has been formed on it, which is not affected by water or air.

Aniline-yellow, when transferred in like manner on transparent objects, lacks intensity. This can only be supplied by repeated coatings, generally, however, at the expense of uniformity.

Aniline-blue may be prepared in several ways. By boiling a shellac solution containing magenta with sodium carbonate, a blue lacquer is obtained, which is, however, little suitable for covering glass or mica, as the lacquer shrinks on drying, owing to the sodic carbonate retaining water. A shellac solution containing magenta, when gently heated on a glass plate, likewise turns blue, but the transparency is impaired by numerous small blisters, and the author recommends the use of pure commercial aniline-blue dissolved in the lacquer, whenever it is desired to coat delicate articles, such as spectacles and other glasses, with a fine blue film.

Magenta produces with shellac a brilliant and perfectly transparent red, provided it has not to be exposed to a high temperature; the colour acquires considerable consistency by an admixture of gum-arabic. It is likewise recommended to employ alcoholic solutions of other resins, such as sandarac, Venice turpentine, &c.

* Dingl. polyt. J., 1871, cc, 224.

Zinaniline prepared from magenta by the action of nitrous acid is employed in a similar manner for the production of yellow lacquers on account of its solubility in alcohol. It cannot, however, be heated above 100° C.

Aniline-brown was not found to yield uniform and transparent lacquers, no matter what resins were employed, the failure perhaps arising from the use of an impure aniline-brown.

Aniline-green, dissolved in alcohol, and added in moderate quantities to the lacquer, produced a bright lustrous and lasting covering; coralline, a lacquer acted upon by the light. Emeraldine and ethylrosaniline green should be dissolved just before being brought together with concentrated lacquer.

Nearly all aniline colours may thus be employed for lacquers, provided they are pure enough, and do not contain too much water. They are for the most part better suited than extracts of dye-woods and other colouring matters, such as indigo, &c. The author obtained remarkably fine colours on glass and mica by employing solutions of gun-cotton in ether mixed with a little alcohol, and coloured by means of small quantities of aniline colours. They leave on evaporation transparent layers, proportionate in thickness to the concentration of the solutions employed. The coating is rendered more elastic by the addition of a little oil of turpentine, and when put on cold glass plates can be detached readily and in a compact form. These coloured collodium skins may be cut into various shapes and figures, and can be fixed firmly by means of a little colourless gum to different transparent objects. Partially etched glass or mica, representing some design or other, may likewise be coated over with coloured lacquers, the etched portions becoming translucent, the others transparent. In case of failure, the lacquer can be readily removed by means of the respective solvents for the resins.

W. V.

On the Ash of Paper resulting from the Burning of the Ministère des Finances, Paris. By E. Chevreul.*

This substance resembles mineral matter rather than a product of organic origin; this results from finely-divided mineral matter which is added to the paper during the process of manufacture.

Paper for writing purposes was formerly made by first preparing the sheets of paper and then sizing them with a mixture of gelatin and alum. The sheet was thus thinly coated with the alumed gelatin and rendered impermeable to ink. By the new process, however, a boiling solution of starch and resinate of soda is intimately

* Compt. rend., lxxiii, 83.

mixed with the pulp, and then a solution of alum is added sufficient to decompose the resinate of soda. An insoluble resinate of alumina is thus produced, and the mixture of the several substances, as homogeneous as possible, constitutes the matter for the paper. The size is, therefore, distributed throughout the thickness of the paper, so that, although the surface be scraped, the paper is still fit to receive the ink, a difference which distinguishes it from paper sized with gelatin. Paper so prepared is much less flexible than that made by the old process, and its inferiority is often much increased by the addition of calcium sulphate, barium sulphate, or kaolin at the time of sizing.

The difference in the sizing of the paper accounts for the fact that paper sized by the old process can be written upon by an indelible ink formed of Indian ink made up with hydrochloric acid to 1 degree of the areometer; whilst with the paper made by the new process it is necessary to make up the Indian ink to the same degree with solution of soda, the acidulated ink not being able to penetrate the latter kind of paper. J. B.

On the Composition of Permanent Illuminating Gas, obtained from the Decomposition of Petroleum Naphtha. By H. H. EDGERTON; with a Prefatory Note by B. SILLIMAN.*

THE conversion of the light naphthas resulting from the rectification of Pennsylvania petroleum into a permanent gas suited for economical use as an illuminant, either by itself or mixed with poor gas or even atmospheric air, is a problem of great importance, since these light naphthas form about one-eighth part of the total production of the crude petroleum. Their employment in this way is of the greater importance, since at present the temptation to use these dangerous volatile hydrocarbons in the adulteration of the petroleum-oils in ordinary domestic use, is very great. At Memphis (Tenessee) and at Fort Wayne (Indiana) these naphthas are utilised according to Rand's modification of Gale's patent. In this process, the vapour of naphtha evolved in a distilling apparatus by a steam-coil is carried into an iron retort heated to redness, where it is in great part converted into permanent gases of very high illuminating power. Small portions of the denser oils which escape destructive distillation are delivered by a syphon into a suitable receptacle, while the gas after cooling is carried to the holder, and is fit for immediate use.

The gas thus obtained is, however, too rich in illuminants to be used alone in ordinary gas-burners; it is, therefore, mixed with ordinary atmospheric air to reduce it to a 25 candle-gas, the amount of air added being about equal to its own volume.

* Am. Journ. Sci. [3], i, 408—411.

The gas as thus supplied at Memphit (Tenessee) has the following composition:—

Hydrocarbon illuminating gases	25·42
Marsh-gas	54·16
Methyl	3·29
Nitrogen	32·24
Oxygen	4·89
	100·00

The author gives several analyses of the gas made at Fort Wayne, by the same process.

C. G.

On the Composition of Milk, and on the Preparation of Artificial Milk. By M. Dubrunfaut.*

After quoting Boussingault's analysis of milk, Payen's observation of the alkalinity of that fluid, and the statement of microscopists that the milk-globules are surrounded by a membrane which is ruptured during the process of churning, the author proceeds to refute the supposed existence of this membrane. He states that if any neutral fat, in a fluid state, be emulsified by water made faintly alkaline, like the serum of fresh milk, globules are obtained precisely similar to those of milk, and that this phenomenon is much more decided if the emulsion be made with a more highly alkaline water containing ·5 to ·6 per cent. of soda. Under these circumstances, the emulsified fat behaves like milk, and an opaline or creamy layer separates on standing. Neutralisation of the alkali causes the fat to rise to the surface, leaving below an oily diaphanous serum.

If we consider that, during the process of churning, the serum, through lactic fermentation, always becomes acid, the inutility of the membrane theory is apparent. To complete the demonstration of such a membrane, it would be necessary to prove that this exercises doubly refractive powers upon light; but it does not do so.

These observations induced M. Dubrunfaut to attempt the preparation of artificial milk, and he claims to have achieved this by emulsifying fatty matters with an artificial serum. This is done as follows:—40 or 50 grms. of saccharine matter (lactin, cane-sugar, or glucose), 20 or 30 grams of dried albumin (the dried white of egg met with in Paris) and 1 or 2 grams of crystals of sodium carbonate, are dissolved in a half litre of water; and the whole is emulsified with 50 or 60 grms. of olive-oil or other comestible fatty matter. The emulsification takes place better at a moderate than at a low temperature.

* Compt. rend., lxxii, 84.

A temperature of 50° or 60° is sufficient. The liquid thus prepared has the appearance of cream, and requires to be mixed with twice its volume of water to acquire the consistence and aspect of milk.

In order to prepare a fluid approaching cream in its properties, gelatin is substituted for albumin. 100 grms. of fat are emulsified in a litre of serum containing 2 or 3 grms. of gelatin. Artificial cream, thus prepared, shows no tendency to separate into fat and serum.

A. Gaudin (*ibid.*, p. 108) comments on Dubrunfaut's proposal, and states that his own observations confirm those of the former chemist as to the deprivation of fats of all unpleasant odour by mere subjection to an appropriate temperature. He further states that very good artificial milk can be prepared from bones rich in fat by purifying this fat by means of superheated steam, and combining with gelatin the fat thus obtained. This milk is, he says almost like that of the cow, and when kept acquires first the odour of sour milk, then that of cheese. The gelatin in it represents the casein; the fat, the butter; the sugar, the sugar of milk. It serves for the preparation of coffee and chocolate, of soups and of creams of excellent flavour, and its cost is but trifling.

Th. Fua (*ibid.*, p. 109) objects to the use of olive-oil in the preparation of artificial milk on the ground that it communicates to this a taste of olives. He states that horse-grease, having an irreproachable flavour, a slight odour of filberts, and being very fluid, is better adapted for the purpose.

A. Sanson (*ibid.* p. 123), controverting an assertion of Dubrunfaut, that his "artificial milk may be profitably employed at all times for the rearing of calves," denies the accuracy of that chemist's conclusion as to the non-existence of an enveloping membrane round the milk globule. After adducing the well-known microscopical reactions of the globules when treated with acetic acid and with ether respectively, demonstrating the existence of the membrane in question, he adds that butters of the first quality are made from milk and from cream which have not undergone the slightest amount of fermentative change.

G. Grimaud (*ibid.*, p. 181) states that milk evaporated to one-sixth of its bulk, keeps well in a vessel simply covered with paper for six months; and he appears to see in this fact an argument for the existence of an enveloping membrane around the milk globule.

Preservation of Eggs. By M. Dubrunfaut.*

The author finds that the best method of keeping eggs for considerable lengths of time, is the well-known one of placing them in milk

* Compt. rend., lxxii, 106.

of lime, rejecting such as do not sink in lime-water, or have cracked shells: for it is found that eggs which do not sink in lime-water undergo certain changes when kept. In seeking for the cause of this difference, Dubrunfaut has arrived at the conclusion that it is dependent on fecundation, the eggs which keep best being fecund. On the other hand, it has previously been noted by other experimenters that the eggs which keep best in the air are those which have not been fertilized. The phenomena of osmose doubtless play an important part in the conservation, as also do the lime and alkaline salts dissolved in the lime-water. T. S.

Miscellanea.

On Coloured (?) Photography. By Dr. Schultz-Sellack. (Dingl. polyt. J., cc, 487—489.)

Copying Drawings by Photography. By G. Meissner. The drawing to be copied is laid face downwards on sensitised paper. Applicable to reproduction of mechanical drawings for distribution. (*ibid.* 489—494.)

Further Experiments on Photographic Copying with Carbonate of Ammonia. By Dr. H. Vogel. (*ibid.* 504.)

Towle's Process for Electroplating the Interior of Metal Pipes. Requires a cut to illustrate the mechanical arrangements, in which all the novelty lies. (*ibid.* cci, 49.)

On the Composition of Crude Tartar. By J. C. Sticht.—Gives the proportions of acid tartrate of potash and of tartrate of lime in several (15) specimens of raw tartar. (*ibid.* cci, 82.)

On the Utilisation of Molybdic Acid for the Colouring of Silk.—Molybdic acid is dissolved in concentrated sulphuric acid to saturation; the liquid heated till white fumes begin to escape; alcohol added; and the silk immediately dyed in the deep blue liquid thereby produced. (*ibid.* cci, 82.)

French Silver Lacquer.—Finely-divided tin, precipitated from its solutions by zinc.

Cadmium Sulphide as a Yellow Colouring for Soap. (*ibid.* 81.)

C. H. G.

Clearing of Muddy Waters.—C. Schloesing repeats the observation that the finely-divided matters suspended in water settle quickly after the addition of a soluble salt. (*ibid.* 81.)

Improvement of Refractory Clays so as to fit them for use in the Manufacture of Glass. By CARL. BISCHOF. (*ibid.* cc, 393—398.)

Concentration of Sulphuric Acid. (Chem. News xxiii, 167; Dingl. polyt. J. cc, 419.)—Observations thereupon. (*ibid.* cci, 45.)

Preparation and Uses of Manganate and Permanganate of Potash. By C. DESCLABISSAC. (Dingl. polyt. J. cc, 58—60.)

Uses of Sodium. Py F. SPRINGMUHL. (*ibid.* cci, 54.)

Use of Glass Vessels in Brewing. (*ibid.* cci, 84.)

Petroleum Production in America. (*ibid.* 85.)

On the Bone-charcoal of Sugar-refineries. By DR. WALLACE. (*ibid.* cci, 159—165.)

Apparatus for the Extraction of Oil from Seeds. By H. VOHL. (*ibid.* cci, 171.)

ERRATA.

Page	Line					
665	14 from top		*for*	dissolve in small quantity	*read*	in small quantity, dissolve
751	4 from bottom		..	amount	..	excess
752	11	..	..	0·030	,,	0·30
764	3	,,	,,	stove	,,	stone
856	23 from top		..	63·866	,,	53·866
,,	32	,,	,,	100·00	,,	107·311

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

On the Influence which the Calcination of some Metallic Oxides exercises on the Heat disengaged in their Reactions. By A. DITTE.*

As a preliminary to the investigation of the influence which the physical state of an oxide has upon the heat disengaged in chemical reactions, the density of magnesia in the bulky form was determined. The magnesia was prepared by calcining magnesium nitrate in an iron vessel containing boiling mercury. The product was a fine white powder, unctuous, and very bulky. A quantity of this substance was introduced into a tared specific gravity flask of about 25 c.c. capacity, and the weight ascertained. The flask was then put under the receiver of an air pump, through the neck of which a pipette with stop-cocks was secured, filled with turpentine specially prepared. A vacuum having been maintained for several hours, the stop-cocks of the pipette were gently opened, and the turpentine was allowed to descend into the flask below. The vacuum was then renewed. After some time the flask was placed on a sand-bath, and slowly heated until the turpentine began to boil, after which it was closed with its stopper and allowed to cool under a bell-jar. By allowing it afterwards to remain in melting ice for an hour, the density at 0° was obtained, and by then subjecting it to the heat of boiling water, the density was again ascertained. From these data, and the known density of the turpentine at 0° and at 100°, the coefficient of expansion, α, between these the two temperatures was calculated by the formula

$$\alpha = \frac{D_0 - D_t}{D_t}$$

This method was found applicable to the other oxides to be considered in the sequel.

Magnesia is amorphous, whatever the temperature of calcination has been. Four modifications have come under the author's observation, differing in density, in expansibility, and in heat of combination. The higher the temperature of calcination, the less the expansibility, whereas the density increases, and the quantity of heat disengaged in combination with sulphuric acid also increases—a fact opposed to the ordinarily received opinion, that the heat evolved by a body diminishes

* Compt. rend., lxxiii, 111; 191—195, and 270.

when its density is increased. The following table gives the principal results obtained in investigating the properties of magnesia:—

Temperature of calcination.	Density at 0°.	Coefficient of expansion from 0° to 100°.	Heat of combination per equivalent.
350°	3·1932	0·0003104	16655
440°	3·2014	0·0002402	18417
Dark red heat	3·2482	0·0001764	19234
Bright red heat	3·5699	0·0001634	20094

When magnesia combines with water, the physical characters of the hydrate are similar to those of the oxide from which it is derived. Hard and dense magnesia gives a similar hydrate, and the heat of combination increases with the density. In general, when one physical property is modified, the others show corresponding variations.

S. W.

On the Influence exerted by the Crystallisation of Cadmium Oxide on its Heat of Combination. By A. Ditte.*

Cadmium oxide is known to occur in two forms. When obtained by calcining the nitrate, it is black and crystalline, but it is yellow and amorphous when formed by combustion of the metal in air, or by calcining the carbonate or hydrate. Ditte finds that these two forms have different heats of combination. The black gives less heat in the calorimeter than the amorphous oxide. The results are shown in the following table:—

		I.	II.	Mean.
Black oxide	For a gram	228·8	230·5	229·6
	For an equivalent	14185	14292	14238

		I.	II.	III.	Mean.
Yellow oxide	For a gram	231·3	235·9	234·9	234·1
	For an equivalent	14342	14631	14567	14513

Thus it would seem that crystallisation deprives a body of a small quantity of potential heat, a result in accordance with the investigations of Favre on the oxidation of carbon and sulphur, and with those of Troost and Hautefeuille on silicon.

S. W.

* Compt. rend., lxxiii, 272.

On the Heat Phenomena which accompany the Transformation of Nitrogen Tetroxide into Nitric Acid, and the Introduction of these two Bodies into Organic Compounds. By L. TROOST and P. HAUTEFEUILLE.*

THIS communication gives the results of experiments instituted to determine the quantity of heat disengaged when nitrogen tetroxide is converted into nitric acid, when the tetroxide is substituted for hydrogen in organic compounds, and in the formation of nitric ethers. The heat disengaged in the conversion of nitrogen tetroxide into nitric acid was first determined and found to be 23,500 heat units for an equivalent. Nitric acid, however, when reduced to hyponitric acid, disengages more heat the greater the concentration; thus acid of the maximum density gives 17,500 heat units; acid of sp. gr. 1·48 gives 17,100; acid of sp. gr. 1·46 gives 16,900; and acid of sp. gr. 1·43 gives 15,300.

The heat disengaged in the reduction of nitric acid (whatever be its state of concentration) in substitution is always much smaller than the total heat observed in the combustion of the substitution-compounds. The following table gives the principal results. The second column of figures shows the heat disengaged by the reduction of the nitric acid employed, as determined in each case:

Products of substitution.	Heat disengaged by an equivalent of the organic body.	Heat disengaged in the reduction of the nitric acid.
Nitrobenzene	38400	16900
Dinitrobenzene	76800	34400
Nitrotoluene	38000	16900
Dinitrotoluene	76000	34400
Nitronaphthalene	36500	15200
Dinitronaphthalene	73000	32300

In the production of nitric ethers the amount of heat disengaged is not so great as with the substitution-compounds. This appears from the following table:—

Nitric ethers.	Heat disengaged by an equivalent.	Heat disengaged by an equivalent of the nitric acid used.
Nitroglycerin	19000	6330
Gun-cotton	52000	10400
Nitromannite	24500	4080

S. W.

* Compt. rend., lxxiii, 378—382.

On the Heat Evolved in the Formation of Organic Derivatives of Nitric Acid. By M. BERTHELOT.*

THE author has determined the amount of heat evolved in the formation of some of the more important nitro-compounds, viz., ethyl nitrate, nitroglycerin, nitromannite, gun-cotton, xyloïdine, nitro-, dinitro-, and nitrochloro-benzenes, nitrobenzoic acid.

I. *Ethyl nitrate.*—In the formation of this ether according to the equation:

$$C_2H_6O + NO_3H = C_2H_5(NO_3) + H_2O.$$

5,800 heat units are disengaged per equivalent of nitric acid; it may be calculated that in its formation from its elements, $C_2 + H_5 + N + O_3 = C_2H_5NO_3$, 65,500 heat units are disengaged; by its combustion with an excess of oxygen, 295,000. The reaction was effected directly in a calorimeter with absolute alcohol and acid of 1·50 sp. gr., and an almost theoretical yield obtained. (A detailed description of the precautions observed is reserved for a special memoir.) It being necessary in the calculation of the experiments to take into account the previous hydration of the acid employed, the solution of the water formed during the reaction in the acid, and the solution of the nitric ether, the amount of each of these corrections was directly determined. The curve obtained for the heat of hydration of nitric acid agrees well with the results of Hess and Thomsen. Similarly the curves for the mixtures of nitric and sulphuric acid, and for the hydration of the nitro-sulphuric acid employed, were experimentally determined.

II. *Nitroglycerin.*—This was prepared in the calorimeter by means of nitro-sulphuric acid, under conditions similar to those lately described by Champion; the yield is four-fifths of the theoretical, secondary reactions being avoided. All corrections being made the normal reaction—

$$C_3H_8O_3 + 3NO_3H = C_3H_5(NO_3)_3 + 3H_2O$$

was found to disengage 13,000 heat units, or 4,300 per equivalent of acid entering into combination. This latter number, which is considerably lower than that for nitric ether, shows that the acid and glycerin have retained almost the whole of their reciprocal energy in the compound, which explains the ready decomposition of nitroglycerin and its formidable effect.

III. *Nitromannite* was prepared by the action of nitro-sulphuric acid; the reaction is slow and lasts a considerable time. Admitting an entire conversion, the numbers obtained give 21,200 heat units for the reaction—

$$C_6H_{14}O_6 + 6NO_3H = C_6H_8(NO_3)_6 + 6H_2O,$$

or 3,500 per equivalent of acid fixed.

* Compt. rend., lxxiii, 260—263.

IV. *Gun-cotton.*—This was prepared by the action of nitro-sulphuric acid, the reaction being stopped at the end of 20 minutes and the product weighed, whereby the amount of acid fixed was determined. It was found each time to amount to 4·5 equivalents. 11,000 heat units were disengaged per equivalent of acid fixed, or 55,000 in the normal reaction—

$$C_{12}H_{20}O_{10} + 5NO_3H = C_{12}H_{15}O_5(NO_2)_5 + 5H_2O.$$

These numbers, compared with those for nitroglycerin, explain the relatively very great stability of gun-cotton. The amount of heat set free in the explosive decomposition of nitroglycerin, calculated on the most probable hypothesis, is about double that evolved by an equal weight of gun-cotton.

V. *Xyloïdin.*—In the reaction—

$$C_6H_{10}O_5 + NO_3H = C_6H_9O_4(NO_3) + H_2O,$$

12,000 heat units are set free, the product being isolated in the solid state.

VI. *Nitrobenzene.*—The normal reaction,

$$C_6H_6 + NO_3H = C_6H_5(NO_2) + H_2O,$$

disengages 36,200 heat units.

VII. *Dinitrobenzene.*—Prepared from nitrobenzene and nitro-sulphuric acid. In the reaction—

$$C_6H_5NO_2 + NO_3H = C_6H_4(NO_2)_2 + H_2O,$$

36,000 heat units are disengaged, the product being solid. Evidently the amount of heat disengaged is proportional to the number of equivalents of acid fixed. Also the amount disengaged in the case of nitrobenzene and other nitro-compounds is far greater than in the case of nitric ether, nitroglycerin, &c. This explains how it is that the explosive energy of the latter is much greater and their stability less; also their comportment as ethers decomposable by potash, with reproduction of the alcohol and acid. Potash, by the action of which on nitric acid only 14,000 heat units are disengaged, cannot yield sufficient energy to reproduce the acid and benzene, whose union to form nitrobenzene gives rise to the evolution of 36,000 heat units; on the other hand, it does possess sufficient energy to cause the decomposition of nitric ether and nitroglycerin, since only from 4,000 to 6,000 heat units are necessary for the regeneration of each equivalent of acid. The number 36,000, for nitrobenzene, is also worthy of note, inasmuch as it is nearly the amount of heat disengaged by the action of hydrogen on nitric acid:—

$$H_2 + NO_3H = NO_2H + H_2O.$$

VIII. *Chloronitrobenzene.*—In the reaction:

$$C_6H_5Cl + NO_3H = C_6H_4(NO_2)Cl + H_2O,$$

36,000 heat units are disengaged. As is well known, two isomeric bodies are formed simultaneously in this reaction; their heat of solution was therefore determined with the mixed product itself.

IX. *Nitrobenzoic Acid.*—

$$C_7H_6O_2 + NO_3H = C_7H_5(NO_2)O_2 + H_2O.$$

Here also about 36,000 heat units are disengaged, which number remains, it seems, almost constant in the nitration of benzene and its immediate derivatives. Toluene, xylene, phenol, mononitrophenol, yield higher numbers; these, however, the author does not quote, as he believes partial oxidation was not avoided.

H. E. A.

On the Compressibility and Dilatation of Gases. By M. Amagat.*

The author compared the coefficients of expansion of sulphurous acid and carbonic acid gases, under constant (atmospheric) pressure, with that of air, between 0° and 250°. The following table gives the results, calculated on the supposition that the coefficient for air has the constant value 0·00367:—

Sulphurous acid.		Carbonic acid.	
0° to 10°	0·004233	At 0°	0·003724
10° to 20°	·004005	,, 50°	·003704
At 50°	·003846	,, 100°	·003695
,, 100°	·003757	,, 150°	·003690
,, 150°	·003718	,, 200°	·003687
,, 200°	·003695	,, 250°	·003682
,, 250°	·003685		

Having thus found that these two bodies first begin to behave as perfect gases at 250°, and even then seem to tend to different limits, he determined to examine how far they departed from the law of Boyle and Mariotte. The initial pressure being that of the atmosphere, he reduced them to one-half of their volume, and found the value of the ratio $\frac{p\ v}{p'\ v'}$ at different temperatures. The following table gives the results of his labours:—

* Compt. rend., lxxiii, 183—186.

Sulphurous acid.		Carbonic acid.	
At 15°	1·0185	At 8°	1·0065
„ 50°	1·0110	„ 50°	1·0036
„ 100°	1·0054	„ 100°	1·0023
„ 150°	1·0032	„ 150°	1·0014
„ 200°	1·0021	„ 200	1·0008
„ 250°	1·0016	„ 250	1·0006

Comparing these values with the coefficients of expansion, he points out that the deviation from the law of Boyle and Mariotte follows nearly the same law as the deviation from the normal co-efficient of expansion. From these results he hopes to be able to ascertain the probable point of liquefaction of those gases which have not hitherto been reduced to the liquid state.

S. W.

On Heat of Neutralisation. By JULIUS THOMSEN.*

In the following table the author gives the numbers of thermal units evolved when one molecule of sulphuric hydrate or an equivalent quantity of another acid, diluted with 400 molecules of water, is neutralised with an equivalent quantity of base in the same state of dilution. Thus, 800 molecules of water enter into the reaction for every molecule of salt formed, except when the want of solubility demands the addition of a larger quantity of water.

The hydrates are represented by putting a horizontal line as many times above the symbol of the radical, as the molecule contains the radical hydroxyl. Thus, $KOH = \bar{K}$; $FeO_3H_3 = \dddot{Fe}$; $C_2H_4O_2 = \bar{Ac}$; $C_2H_2O_4 = \ddot{O}$; $C_4H_6O_4 = \ddot{Su}$, &c. The formulæ of reaction, as ($KOHAq$, $ClOHAq$) or (BaO_2H_2Aq, SO_4H_2Aq), &c., become therefore ($\bar{K}Aq$, $\bar{Cl}Aq$), ($BaAq$, SO_2Aq), &c.

The author has determined the heat evolved for the different degrees of neutralisation, but has in these tables given only the results referring to the formation of neutral salts.

In the tables the total heat as obtained by experiment is given; but it must be remarked that when, as with barium, the salt formed is insoluble, the total heat evolved is in reality the sum of the heat of neutralisation and of the heat of precipitation. The author has shown in other papers how this heat of precipitation can be eliminated from the results given below.†

* Deut. Chem. Ges. Ber. iv, 586–590.

† The author remarks that in another paper of his (of which an abstract has been given on page 473 of this volume) some numbers given are inexact, but that the general result is not thereby affected.

TABLE I.

R.	Sulphuric acid (R,H_2SO_4Aq).	Hydrochloric acid ($R,2HClAq$).	Nitric acid ($R,2HNO_3Aq$).	Acetic acid ($R,2C_2H_4O_2Aq$).
2 $\overline{Li}Aq$	31290	27700	—	—
2 $\overline{Na}Aq$	31380	27490	27360	26370
2 $\overline{K}Aq$	31290	27500	27540	26430
2 $\overline{Tl}Aq$	31130	44340*	—	—
2 $\overline{N}Ac_4Aq$	31010	—	—	—
$\overline{Ba}Aq$	36900*	27780	28260	26900
$\overline{Sr}Aq$	30710	27630	—	—
$\overline{Ca}Aq$	31140	27900	—	—
$\overline{Mg}$	31220	27690	27520	—
2 $\overline{N}H_3Aq$	28150	24540	24640	—
2 $\overline{N}Ac_3Aq$	28340	25040	—	—
$\overline{Mn}$	26480	22950	—	—
$\overline{Ni}$	26110	22580	—	—
$\overline{Co}$	24670	21140	—	—
$\overline{Fe}$	24920	21390	—	—
$\overline{Cd}$	23820	20290	20320	—
$\overline{Zn}$	23410	19880	—	18030
$\overline{Cu}$	18440	14910	14890	12820
$\overline{Pb}$	21060*	14360*	15340	13120
$\overline{CuO}$	18800	15270	15250	13180
$\overline{HgO}$	—	19420	—	—
$\overline{PbO}$	23500*	16790*	17770	15460
$\overline{Ag_2O}$	14490	42380*	10880	—
$\frac{2}{3}$ $\overline{Al}$	20990	18640	—	—
$\frac{2}{3}$ $\overline{Be}$	16100	13640	—	—
$\frac{2}{3}$ $\overline{Cr}$	16440	13730	—	—
$\frac{2}{3}$ $\overline{Au}$	—	13680	—	—
$\frac{2}{3}$ $\overline{Fe}$	11250	11150	11200	7990

* In the cases marked by the asterisk, the salt formed is insoluble, or almost insoluble, so that either the whole or part of the heat of neutralization has to be added to the heat of precipitation.

TABLE II (R,QAq).

R.	Q.				
	Hyposulphuric acid, $H_2S_2O_6$.	Sulphovinic acid, $2HC_2O_5.SO_4$.	Chloric acid, $2HClO_3$.	Hypophosphorous acid, $2(H.PH_2O_2)$.	Hydrogen sulphide, $2(H.SH)$.
2 NaAq	27070	26930	27520	30320	15480
2 NH_3Aq	—	—	—	—	12390
BaAq	27760	27560	28050	30930	15750
Mg	27540	—	—	—	—
Co	—	21120	—	—	—
Cd	20360	—	—	—	—
Cu	—	14840	15550	—	—
$\frac{2}{3}$ Fe	—	—	10700	—	—

TABLE III.—*Normal Sodium Salts.*

Q.		(2NaAq,QAq.)
Hydrofluoric acid	$2(H.Fl)$	32540
Sulphuric acid	$H_2.SO_4$	31380
Selenic acid	$H_2.SeO_4$	30390
Hypophosphorous acid	$2(H.PO_2H_2)$	30320
Sulphurous acid	$H_2.SO_3$	28970
Metaphosphoric acid	$2(H.PO_3)$	28750
Phosphorous acid	$H_2.PO_3H$	28370
Oxalic acid	$H_2.C_2O_4$	28280
Hydrochloric acid	$2(H.Cl)$	27480
Hydrobromic acid	$2(H.Br)$	27500
Hydriodic acid	$2(H.J)$	27350
Chloric acid	$2(H.ClO_3)$	27520
Nitric acid	$2(H.NO_3)$	27360
Hyposulphuric acid	$H_2.S_2O_6$	27070
Selenious acid	$H_2.SeO_3$	27020
Chloroplatinic acid	$H_2.PtCl_6$	27220
Hydrofluosilicic acid	$H_2.SiFl_6$	26620
Sulphovinic acid	$2(H.C_2H_5.SO_4)$	26930
Formic acid	$2(H.CHO_2)$	26400
Acetic acid	$2(H.C_2H_3O_2)$	26310
Pyrophosphoric acid	$\frac{1}{2}(H_4.P_2O_7)$	26370
Orthophosphoric acid	$H_2.PO_4H$	27080
Orthoarsenic acid	$H_2.ASO_4H$	27580
Citric acid	$\frac{2}{3}(H_3.C_6H_5O_7)$	25470
Tartaric acid	$H_2.C_4H_4O_6$	25310
Succinic acid	$H_2.C_4H_4O_4$	24160
Chromic acid	$H_2.CrO_4$	24720
Carbonic acid	$H_2.CO_3$	20180
Boric acid	$H_2.B_2O_4$	20010
Hypochlorous acid	$2(H.ClO)$	19370
Hydrosulphuric acid	$2(H.SH)$	15480
Hydrocyanic acid	$2(H.Cy)$	5530
Stannic acid	$\frac{1}{2}(H_4.SnO_4)$	4780
Silicic acid	$\frac{1}{2}(H_4.SiO_4)$	2710

R. S.

On the Inaccuracy of Favre and Silbermann's Thermochemical Determinations made with the Mercury Calorimeter. By JULIUS THOMSEN.*

THE fact that almost all the author's determinations of the heat of neutralisation are lower than those which Favre and Silbermann have made with the mercury calorimeter, seems to indicate that although that apparatus may be useful for comparative, it is useless for absolute determinations. The author gives a table of the differences between his own results and those of Favre and Silbermann (Table II below), and points out, as a decisive argument against their apparatus, that several numbers determined by him according to three different methods, have been found to agree well with each other, but to differ from those obtained with the mercury calorimeter.

For instance, the difference of the heat evolved when sulphuric acid is neutralised with certain bases (HKO, HNaO, NH_4HO), from that evolved by hydrochloric acid on neutralisation with the same bases, has been determined by the author—1st, by direct neutralisation; 2nd, by decomposition of the sulphates of those bases with barium chloride; 3rd, by partial decomposition.†

The following Table exhibits these differences, as compared with those which would follow from Favre and Silbermann's results:—

TABLE I.

Method.	Sodium Hydrate.	Potassium Hydrate.	Ammonium Hydrate.
Neutralisation	3890	3784	3608
Double decomposition	3872	3832	3704
Partial decomposition	3852	3807	3608
Mean	3871	3807	3673
Favre and Silbermann	1364	854	2308

The next table contains the numbers of thermal units by which Favre and Silbermann's determinations of the heat of neutralisation for the reaction (R, Q, aq) differ from those of the author.

* Deut. Chem. Ges. Ber., iv, 591. See further p. 597 of the same Journal, where the author replies to the observations of H. Ste. Claire Deville (Bull. Soc. Chim. [2], xiv, 5) who maintains the accuracy of Favre and Silbermann's mercury calorimeter.

† Pogg. Ann., cxxxviii, 504.

TABLE II.

R.	Q.			
	H_2SO_4.	2HCl.	$2HNO_3$.	$2C_2H_4O_2$.
2 NaAq	+ 240	+ 2766	+ 3206	+ 830
2 KAq	+ 876	+ 3812	+ 3480	+ 1516
BaAq	+ 4486	+ 2824	+ 2460	− 396
2 NH_3Aq	+ 1230	+ 2532	+ 2712	—
Mg	− 2340	− 1250	− 1840	—
M	− 2330	− 485	—	—
Ni	− 2246	− 1756	—	—
Co	− 1110	− 392	—	—
Fe	− 3176	− 1734	—	—
Cl	− 3340	− 4072	− 4088	—
Zn	− 2500	− 3266	− 3184	− 2590
Cu	− 3000	− 2078	− 2060	− 2292
PbO	− 776	+ 5756	+ 710	+ 1216
Ag_2O	—	+ 3556	+ 1532	—
$\frac{2}{3}$ Al	+ 906	—	—	—
$\frac{2}{3}$ Fe	+ 2222	—	—	—

R. S.

On the Length of Time required for the Evaporation and Condensation of Solid Bodies. By ALEXANDER NAUMANN.*

THE vapour-tensions of carbon trichloride and of naphthalene have been examined with Hofmann's apparatus for the determination of vapour-densities, modified in such a manner that on heating, as well as on cooling, it quickly attained a constant temperature. It was observed that, in the case of both vapours, the tension became constant two minutes, or at the most five minutes, after the commencement of the passage of steam, alcohol-vapour, or water of 15° through the surrounding cylinder. From this the author infers that the time of evaporation and of condensation of solid bodies in a vacuum is very short.

The following results, approximate with regard to the vapour-tensions, are given:—

Tension at 15°.		Tension at 78°.	Tension at 100°.	Boiling point.	Melting point.
C_2Cl_6	1 mm.	13·5 mm.	31 mm.	182°	160°
$C_{10}H_8$	2 mm.	9 mm.	20·5 mm.	218°	79·2

R. S.

* Deut. Chem. Ges. Ber., iv, 646.

On the Theory of Dissociation. By A. HORSTMANN.*

THE author traces the connection between the temperature, pressure, and the other elements which are of influence in a case of dissociation lately examined by H. St. Claire Deville. When steam acts upon iron in a closed vessel, there exists at every temperature a tendency towards the establishment of a constant ratio between the partial pressures of the steam and of the hydrogen which, while dependent upon the temperature, appears to be independent of the quantity of iron and its oxide, and of the absolute pressure of the gases. This may be explained by Pfaundler's hypothesis that in a given time there are as many molecules of water decomposed as newly formed. The author considers it admissible to suppose that, at the moment when these two reactions take place, a molecular compound $FeOH_2$ is formed, which, however, according to temperature or other circumstances, is immediately split up again either into $Fe + H_2O$, or into $FeO + H_2$. If such a compound were formed, then according to the mechanical theory of heat, the pressure of the hydrogen and that of the steam would increase according to the same law, which can be expressed by the equation—

$$dp = dT \frac{Q}{AT\delta v},$$

where A represents the mechanical equivalent of heat, T the absolute temperature, δv the volume of the liberated gas, Q the quantity of heat consumed in the process of decomposition, and dp the increment of pressure. δv remains the same for steam and hydrogen. Q can be computed from the heats of combustion. By the combination

of 16 pts. of oxygen with iron, are evolved	66,100	thermal units.
,, ,, ,, hydrogen ,,	59,200	,,
so that the difference	6,900	

shows how much more heat is consumed when H_2O instead of H_2 is separated from the compound $FeOH_2$. Q, and consequently dp, is greater in the case of steam. Calling the pressure of the hydrogen p_1 and that of the steam p_2, we see that p_2 increases faster than p_1 and that the ratio $p_1 : p_2$ diminishes as the temperature rises; and this is confirmed by experiment.

If it be supposed that the quantity of heat which, during the process of decomposition, is consumed for internal work (this quantity, in the case of hydrogen, being called U, and in the case of iron U_2) does not vary with the temperature, then another equation can be deduced—

* Deut. Chem. Ges. Ber., iv, 635.

$$\log \frac{p_1}{p_2} = C - \frac{U}{AR} \cdot \frac{1}{T},$$

in which $R = s_0 \frac{760}{273}$, s_0 being the molecular volume of H_2 or of H_2O, and $U = U_1 - U_2$. The unknown quantities C and U can be determined by two observations, and then the above equation will furnish the value of $\frac{p_1}{p_2}$ for every temperature.

The following table shows how far the experimental values agree with those obtained by calculation from the equation:—

Temperature.	Found.	Calculated.
200°	20·49	23·07
265°	13·96	14·01
360°	8·62	8·11
440°	5·75	5·75
860°	2·34	2·08
1040°	1·74	1·65
1600°	0·92	1·06

The value of U is found from the above equation to be — 3900 heat units instead of —6900, which number would directly follow from the known heats of combustion of hydrogen and iron. But considering the sources of error to which the determinations of the heats of combustion, as well as of the ratio $\frac{p_1}{p_2}$ are subject, we must be contented that the value of U, whether obtained directly or indirectly, has the same sign and is of the same order.

R. S.

On the Influence exerted in the Voltaic Battery by the Size of the Plates. By Th. du Moncel.*

The author proposes to himself two questions: 1st, whether the wear and tear of zinc and exciting liquid in a battery, occasioned by increasing the electro-positive plate, is balanced by the advantage which accrues in overcoming resistance; and 2ndly, whether, if the surface of the electro-negative plate is increased, the feebleness of intensity produced by a small electro-positive plate will be compensated. To the first question he answers, that it depends essentially on the circuit. If the resistance be great, experiment shows that the intensity of the current is but little affected; but when the circuit has a small resistance, the resistance of the battery cannot be neglected, and may preponderate. To reply to the second question, he has had recourse to a

* Compt. rend., lxxiii, 436—440.

series of experiments, which show that it is advantageous to increase the electro-negative plate, not only for economy, but for intensity and permanency of action.

S. W.

On the Transport of Salts by the Electric Discharge. By M. Becquerel.

In this communication Becquerel shows that only certain salts are transported by the electric discharge, and these only in one direction, namely, from the negative electrode to the positive, and not, as would have been supposed, from the positive to the negative. In his experiments he has made use of an ordinary electrical machine and of an induction coil, taking care that the spark was not of such intensity as to decompose the bodies under examination. Pieces of paper saturated with solutions of the salts were so connected with the electrodes of the machine, that a discharge could be passed from one to the other. Thus a slip of paper moistened with a solution of ferrous sulphate was placed on a platinum plate in connection with the machine. At a distance of one or two centimetres from this, another slip of paper moistened with a saturated solution of potassium ferricyanide, was attached to a platinum ball in connection with the earth. When the machine was put in action, a blue precipitate was formed on the ferrous sulphate, and none on the potassium salt. When the operation was performed inversely, no precipitation took place. Other bodies were examined in like manner, and the following were found to be transported from the negative to the positive electrode, and not in the opposite direction:—

Potassium ferricyanide	Sulphuric acid
Potassium dichromate	Phosphoric acid
Barium chloride	Ammonium chloride
Sodium chloride	Ferrous chloride.
Potassium chloride.	

The following substances were not transported, whichever might be the direction of the current:—

Cobalt chloride	Platinum chloride
Silver nitrate	Potassium hydrate
Potassium sulphate, &c., &c.	

S. W.

Second Memoir on the Decoloration of Flowers and Leaves by Electric Discharges. By M. BECQUEREL.*

THE action of temperatures varying from — 15° up to 100° upon the coloured tissues of plants has given results similar to those obtained by the action of feeble currents of electricity, described in a former paper.† Thus the petals of red flowers, such as the poppy, when exposed to a temperature of — 12° to — 15° for half an hour, assume a violet tint; the leaves of the *Begonia discolor*, which are green on the upper and red on the lower surface, show effects of the same kind; at first an infiltration of the colouring matter takes place, the upper surface becoming of the same colour as the lower; gradually the green colour of the upper surface becomes visible, until after a certain time both sides of the leaf present the same tint; if the action be continued, the colour of the chlorophyll partially disappears.

At zero the petals and leaves experimented on do not appear to undergo any change, and it is only when the temperature is raised to from 50°—60°, that the phenomena of decoloration begin to manifest themselves in the same manner as before described. If a petal which has taken a violet colour from exposure either to a high or low temperature is placed in water rendered slightly acid with acetic acid, it recovers its original red colour; if, on the contrary, it is placed in water containing a little ammonia, the violet colour becomes more pronounced.

In the three methods, it appears that an alteration of the envelopes of the cells takes place, which allows the coloured liquid to diffuse to the exterior; on examination by the microscope, however, no change in the structure can be detected; a chemical change, attended with destruction of the red colouring matter, must also have taken place.

The petal of a poppy when rubbed in a mortar with a little water, gives, on slight pressure, a violet-coloured liquid, instead of a red liquid, as might have been expected; the liquid obtained has the same tint as that of a petal which has been electrified. Pieces of paper coloured with this liquid, and exposed to the action of electricity, do not alter in tint, but gradually become white. Red and yellow flowers do not act precisely as red flowers; electricity easily destroys their colouring matters, but it does not act by first rendering them soluble in water, as is the case with the violet produced from the red flowers.

A. P.

* Compt. rend., lxxiii, 302—306.

† Journ. Chem. Soc. [2], ix.

Elementary Deduction of the Fundamental Equation of the Dynamical Theory of Gases. By L. PFAUNDLER. (Wien. Acad. Ber. lxiii [2], 159–169.)

On Motion and Equilibrium, with special reference to the Diffusion of Gaseous Mixtures. By J. STEFAN. (Ibid. 63, 124.)

On the Theory of the Molecular Motions of Gases. By J. THOMSEN. (Deut. Chem. Ges. Ber. iv, 595.)

The Physical Characters of Carbonic Acid, a Contribution to the Theory of Gases. By G. RECKNAGEL. (Pogg. Ann. Ergänzungsband, v, 563—592.)

Relations between Atomic Weights. By F. WREDEN. (Ibid. 571—574.)

Apparatus for the convenient Arrangement of Certain Combinations of Galvanic Elements. By C. BOHN. (Pogg. Ann. Ergänzungsband, v, 648—653.)

Action of the Secondary Currents of the Voltaic Battery on the Primary Currents, and on one another. By P. RIESS. (Pogg. Ann. cxliii, 195—211.)

Refraction relations of Fuchsine. By O. CHRISTIANSEN. (Ibid. 250—257.)

On Anomalous Dispersion. By A. KUNDT. (Ibid. 259—269.)

Anomalous Dispersion of acute-angled Prisms. By V. v. LANG. (Ibid. 269—272.)

Abnormal Sequence of Colours in the Spectra of certain Substances. By SELLMEIER. (Ibid. 272—282.)

Anomalous Dispersion of certain Substances. By L. SORET. (Ibid. 325—328.)

Note on the Spectrum of Uranus and the Spectrum of Comet I., 1871. By W. HUGGINS. (Proc. Roy. Soc. xix, 488.)

Inorganic Chemistry.

The Action of Hydrogen upon Nitric Acid. By E. BOURGOIN.*

As the result of a series of electrolytic researches previously published, the author has shown that there is satisfactory ground for assuming that when nitric acid is diluted with a considerable quantity of water, a hydrate of the formula $N_2O_5.4H_2O$ is produced; notwithstanding that H. St. Claire Deville, from an examination of the action of zinc upon nitric acid, has assigned to the same body the formula $N_2O_5.2H_2O$. When this acid, in different degrees of concentration, is submitted to the action of the electric current, it is supposed to undergo decomposition in the following manner:—

$$N_2O_5.4H_2O = (N_2O_5 + O_4) + 4H_2.$$

oxygen gas alone being evolved at the positive pole, while the acid steadily concentrates at the same point. At the negative pole hydrogen is set at liberty, but this gas, finding itself at the moment of liberation in presence of a certain amount of nitric acid, reacts upon the latter, with results varying according to the concentration of the acid. The examination of this latter action is more especially the subject of the present paper.

I. When a very dilute solution, previously freed by boiling from dissolved oxygen, is submitted to electrolysis, pure hydrogen alone is evolved at the negative pole; the nitric acid during the whole period of the experiment not being sensibly affected by the nascent gas. The analytical results confirm this assertion.

II. When the solution is less dilute, corresponding nearly to the formula $N_2O_5.2H_2O + 12{\cdot}5$ Aq., the hydrogen evolved, at first pure, soon contains a small quantity of nitrogen, and towards the termination of the experiment, ammonia may be detected in the decomposing cell.

* J. Pharm. [4], xiii, 266—270.

III. With a solution one-fourth of the preceding strength, $N_2O_5.2H_2O$, 38 Aq., hydrogen only can be collected at the commencement, as in the previous instance; the gas, however, soon contains nitrogen, which latter increases gradually, till, having attained a maximum, it finally disappears. This reaction is explained by the fact that, during the experiment, the acid, becoming gradually weaker, is at length no longer able to evolve nitrogen. The liquid was carefully examined for nitrous oxide, which, owing to its ready solubility, would have remained in solution, but the results in this particular case were always negative.

IV. When the solution is much more concentrated, containing only 15 eq. of water, no hydrogen is evolved from the negative pole, although oxygen is freely liberated from the positive pole; the whole of the hydrogen set at liberty reacts upon the acid, and the products of this reaction remain at first dissolved. The solution surrounding the negative pole soon acquires a blue coloration, and then hydrogen, mixed with a small quantity of nitrogen, is slowly liberated. After some hours a new gas appeared, which gradually, but completely replaced the hydrogen, and finished by disappearing in its turn, as shown in the accompanying table. The gas proved to be nitric oxide.

Gas collected.	1 hour.	12 hours.	15 hours.	20 hours.	30 hours.	48 hours.	50 hours.
Hydrogen	98·96	92·5	—	69·1	83·1	98·6	100·
Nitrogen	1·04	3·5	1·4	3·4	10·1	1·4	—
Nitric oxide ..	—	4·0	98·6	27·5	6·8	—	—

Towards the termination of the experiment, the negative liquid contained a considerable quantity of ammonia, and possessed, moreover, the characteristics of an aqueous solution of nitrous acid; it reduced permanganate of potassium and chloride of gold, and when neutralized with an alkali, not only blackened a solution of ferrous sulphate, but disengaged ruddy vapours upon the addition of dilute sulphuric acid.

V. When the pure acid, $N_2O_5.4H_2O$ is electrolysed, the evolution of gas, at first *nil*, soon becomes extremely rapid, and the gas which is collected is entirely absorbable by a solution of ferrous sulphate; it is pure nitric oxide. After a while hydrogen makes its appearance, when the liberation of nitric oxide slowly ceases.

The foregoing gaseous mixtures were analysed by mixing them with oxygen, and then adding a solution of caustic potash; the excess of oxygen having been removed by pyrogallic acid, the hydrogen was determined by explosion in the usual way. In conclusion, the author

states that these experiments show that nitrous acid, nitric oxide, nitrogen, and ammonia result from the reducing action of hydrogen upon nitric acid, and that they furnish additional evidence of the energetic action of hydrogen gas, when the latter is capable of exerting its power in the nascent state.

J. W.

Action of Iodine upon Insoluble Sulphides. By E. FILHOL and J. MELLIÈS.*

CERTAIN facts which presented themselves during the analysis of sulphuretted waters by means of iodine, induced the authors to study more closely the action of this element upon the metallic sulphides. In the present instance they confine themselves solely to its action upon insoluble sulphides, employing for the purpose both natural and artificially prepared compounds.

Sulphide of zinc, obtained by decomposing a solution of zinc acetate with hydrosulphuric acid, is rapidly decomposed by dry iodine at the ordinary temperature, zinc iodide being produced, while sulphur is set at liberty. The reaction commences instantly, and the mass becomes sensibly warm; the decomposition, however, under these circumstances is never quite complete, even in presence of a large excess of iodine, but the sulphide is entirely destroyed if the mixture be placed in a tube hermetically sealed, and heated for a short time to a temperature of 200°. When iodine is thrown into water containing sulphide of zinc in suspension, the action, at first slow, gradually increases, according as the zinc iodide already formed permits a larger quantity of iodine to pass into solution. The action is very rapid when the water is raised to its boiling point, a few minutes sufficing to effect complete decomposition of the sulphide. As in the former instance, almost the whole of the sulphide is transformed into iodide, but a slight secondary reaction ensues, which results in the formation of a small quantity of sulphate; 100 pts. of sulphide yield 98·5 pts. of iodide and 1·5 pt. of sulphate, the phenomenon of oxidation being due to the decomposition of water, with formation of traces of hydriodic acid. The action of alcoholic or ethereal solutions of iodine upon zinc sulphide is as energetic as when water is employed, while the proportion of sulphate produced under these circumstances is very small, and disappears entirely when carbon disulphide is employed as a solvent for the iodine.

When finely pulverised zinc-blende is used instead of the artificial sulphide, the action proceeds with extreme slowness at the ordinary temperature, but in a sealed tube at a temperature of 200° the decom-

* Ann. Chim. Phys. [4], 58—64.

position is rapidly complete; a small quantity of sulphate likewise results during this reaction.

The sulphides of manganese and cadmium and ferrous sulphide behave towards iodine in a manner precisely similar to sulphide of zinc; but ferric sulphide and white pyrites are decomposed in presence of excess of iodine, with formation of *ferrous iodide*, one equivalent of iodine replacing one-half and two equivalents of sulphur respectively. The authors pertinently remark that it is a very unexpected observation that the ferrous salt should remain stable in presence of a considerable excess of iodine.

The sulphides of nickel, cobalt, and bismuth, and the native sulphide of antimony, are decomposed slowly in the cold, but rapidly at 200°. The artificial antimony sulphide is also attacked by dry iodine, and in presence of water, this latter reaction results in the formation of oxyiodide of antimony and hydriodic acid.

Artificial stannous sulphide is easily decomposed in the cold by powdered iodine, the temperature of the mixture rising to such a degree that a portion of the iodine is volatilised. Stannous iodide is formed, which, if alcohol has been employed, may be obtained in long needle-shaped crystals. Stannic sulphide (*aurum musivum*) is, on the contrary, but slowly attacked in the cold by iodine, whatever solvent be employed for this body; the action is complete at 200°, with formation of stannic iodide.

The two sulphides of arsenic react very quickly with iodine at the ordinary temperature, the mixture becoming liquid at 80°. The composition of the iodides resulting from this reaction has not yet been satisfactorily ascertained. When artificial sulphide of lead is mixed with dry iodine, an instantaneous reaction takes place, attended with a sublimation of a small quantity of the iodine; iodide of lead is immediately formed, as indicated by its characteristic yellow colour, but no sulphate is produced in this reaction, even when it is effected in presence of water. Galena is similarly attacked, but with greater difficulty. Both copper pyrites and the artificial sulphide are decomposed under the influence of iodine, with production of insoluble cuprous iodide, but the pyrites require a temperature of at least 200°. Since the iodide of iron produced in this manner is soluble, the reaction may be utilized for the analytical separation of the copper and iron contained in this mineral.

Mercurous sulphide, or at least the precipitate which is obtained by passing a current of sulphuretted hydrogen gas through a solution of mercurous nitrate, undergoes very rapidly the action of iodine, but mercuric iodide is formed. This fact may be considered as an argument in favour of the views of those chemists who do not admit the existence of a mercurous subsulphide. Mercuric sulphide, vermilion,

and cinnabar, are equally decomposed by iodine at different temperatures, with production of mercuric iodide.

Finally, the sulphides of gold and platinum are slowly, and the sulphide of silver energetically, decomposed by iodine, with deposition of sulphur, and production of the corresponding metallic iodide.

The authors propose to apply some of the foregoing reactions to effect the analytical separation of certain metals in those cases in which the sulphides are more or less easily decomposable by iodine, or when the iodides formed are soluble or insoluble in water. Thus the analysis of a mixture of zinc-blende and galena is an easy operation, owing to the insolubility of lead iodide in cold water, and copper may be separated in a similar manner from all metals forming soluble iodides, since its iodide is a perfectly definite and insoluble compound.

J. W.

On the Temperature of Decomposition of Hydrogen Sulphide. By J. Myers.*

The reaction between boiling sulphur and steam has been experimented on, and the results published in the Journal für praktische Chemie, cviii, 123. The conclusion drawn from these experiments was that hyposulphurous acid, the production of which, under these circumstances, most Hand-books deny, was probably formed, but that no pentathionic acid was produced. This reaction is therefore analogous to that of sulphur upon the alkalis.

From calculations as to the number of heat-units required in the reaction, it may be safely asserted that the reaction must take place below 400°, and that the decomposition temperature of hydrogen-sulphide cannot be higher than this. In most text-books it is said that the gas first begins to decompose at a red heat; but experiments have shown that although the gas is not decomposed at the temperature of boiling mercury, it begins to suffer decomposition at 400°, and is decomposed rapidly at the boiling point of sulphur. Myers places the decomposition-point of hydrogen sulphide between 350 and 400°, probably nearer to the lower temperature. The experiments were made with the gas made from ferrous sulphide, which generally contains hydrogen; they were also repeated with pure gas from antimonious sulphide, but with exactly the same result.

A. P.

On Hydrogen Sulphide containing Arsenic. By J. Myers.†

In the experiments described in the decomposition of hydrogen sulphide evolved from ferrous sulphide and sulphuric acid, it was found that in

* Ann. Ch. Pharm., clix, 124—127. † Ann. Ch. Pharm., clix, 127.

passing this gas through a tube placed in boiling mercury, an orange-coloured deposit was formed in the heated tube. This on analysis proved to be a sulphide of arsenic. The gas must therefore have contained a volatile arsenic compound, probably arsenetted hydrogen; this compound, then, is not decomposed by hydrogen sulphide at ordinary temperatures, but at a higher temperature the decomposition takes place. The arsenic arose from the sulphuric acid, the arsenic compound in which must have been acted on by nascent hydrogen produced by the impure ferrous sulphide. A direct experiment showed that nascent hydrogen has the power of reducing arsenious sulphide and arsenic acid. This observation has its importance in judicial investigations. The author thinks it possible that the traces of arsenic said to be found in animals may have their origin in this source.

A. P.

Potassium-amalgam and Sodium-amalgam. By K. KRAUT and O. POPP.*

WHEN sodium-amalgam containing 3 per cent. of sodium is left in contact with a solution of caustic potash or potassium carbonate, hard shining cubes with octohedral and dodecahedral faces make their appearance. They contain 98—98·4 per cent. of mercury and varying quantities of potassium (0·93—1·56 per cent.) and sodium (0·036—0·64 per cent.).

By using a solution of caustic soda or sodium carbonate, long needles are obtained, the mean composition of which is 98 per cent. of mercury and 1·84 per cent. of sodium.

C. S.

On certain Chromium Compounds. By JULIUS HEINTZE.†

WHEN gaseous ammonia acts on dry powdered potassium chlorochromate, there is produced, by coalescence of several molecules, a compound of the formula, $Cr_3O_3(OK)_2$. Potassium amidochromate, crystallisable from water in garnet-red prisms, is obtained by the action of ammonia gas on potassium chlorochromate in presence of pure ether.

Chromyl chloride treated with diluted ammonia gas is reduced with incandescence to chromium oxide, no diamide of chromic acid being produced; dissolved in glacial acetic acid, ammonia gas only yields chromium acetate, and with chloroform a non-crystalline ammonia salt.

Potassium chlorochromate and potassium cyanide yield gaseous cyanogen chloride and yellow potassium chromate; with nitrogen tetroxide, nitryl chloride, NO_2Cl, is produced. The corresponding

* Ann. Chem. Pharm., clix, 188—191. † J. pr. Chem. [2], iv, 58.

bromide is obtainable by the action of nitrogen tetroxide on potassium bromochromate, formed by dissolving potassium dichromate in bromine water. C. R. A. W.

On the Action of Sulphurous Acid on Platinic Chloride. By K. BIRNBAUM.*

IN a former communication† the author has shown that platinic chloride is reduced by sulphurous acid to platinous chloride, and that the chlorine in the latter compound can be replaced by the group HSO_3, NH_4SO_3, and so on. By the action of sulphurous acid on ammonio-platinic chloride, platino-chlorosulphurous acid is formed, which crystallises in yellow needles. A sodium salt formed by neutralizing with sodic hydrate is obtained by careful evaporation of the solution without heat, and by recrystallisation, in small transparent orange-coloured needles, which are very deliquescent. This salt has the formula, $Pt\begin{matrix}Cl\\NaSO_3\end{matrix}2NH_4Cl + H_2O$. The calcium and magnesium salts can also be obtained; they are excessively deliquescent, and crystallise in small needles. If the acid is neutralized with barium hydrate and gradually evaporated, a white precipitate separates, which consists almost entirely of barium sulphite; on further evaporation of the clear liquid, small groups of beautiful red-yellow crystals appear which have the formula—

$$\begin{matrix}Pt\left\langle\begin{matrix}Cl\\SO_3\end{matrix}\right.\\Pt\left\langle\begin{matrix}SO_3\\SO_3\end{matrix}\right.\\Pt\left\langle\begin{matrix}SO_3\\Cl\end{matrix}\right.\end{matrix}\Big\rangle Ba.BaCl_2.6NH_4Cl + 3H_2O.$$

In his former memoir, already referred to, the author assigned to a salt the formula, $Pt\begin{matrix}HSO_3\\HSO_3\end{matrix}2NH_4Cl + H_2O$; it is probable, however, that this compound was merely an impure specimen of one of the following salts:—Ammonium chloroplatinate dissolves in a solution of acid ammonium sulphite with the aid of gentle heat, and by careful evaporation beautifully formed colourless prisms are obtained which seem to have the composition, $Pt\begin{matrix}Cl\\HSO_3\end{matrix} \cdot \begin{matrix}NH_4\\H\end{matrix}SO_3 + 4H_2O$. If potassium carbonate is added to a solution of the above, rapid evolution of carbonic anhydride takes place; and the neutral liquid on evaporation yields colourless, brilliant, but very deliquescent crystals, which, when dried over sulphuric acid, have the composition, $Pt\begin{matrix}Cl\\KSO_3\end{matrix} \cdot \begin{matrix}NH_4\\K\end{matrix}SO_3 + 3H_2O$.

* Ann. Ch. Pharm. clix, 116—124. † Ibid., clii, 137.

By the action of acid ammonium sulphite on platinochlorosulphurous acid in which already one atom of chlorine is replaced by HSO_3, the second atom of chlorine may be replaced, and a body of the formula, $Pt\begin{matrix}NH_4SO_3\\NH_4SO_3\end{matrix} . 2NH_4Cl$, produced. In appearance it cannot be distinguished from the substance before described. When sulphurous anhydride is passed into a solution of ammonium sulphite with ammonium chloroplatinate and then neutralized with sodium carbonate, the difficultly soluble compound, $PtSO_3.3Na_2SO_3$ is obtained, described by Litton and Schnedermann; the author considers the true formula of this body to be $Pt\begin{matrix}NaSO_3\\NaSO_3\end{matrix} . 2Na_2So_3$. All the above salts yield, on treatment with concentrated hydrochloric acid and potassic chloride or ammonic chloride, the well-known platinum double salts.

A. P.

Mineralogical Chemistry.

Note on Montebrasite. By M. Des Cloizeaux.*

A new mineral obtained from Montebras (Creuse) has the composition of fluophosphate of aluminium, sodium, and lithium. The author proposes to call it montebrasite. It is abundantly diffused with the other phosphates of aluminium, such as wavellite and turquoise, in the stanniferous strata of Montebras. In its composition, and in some of its physical characters, it offers certain analogies to amblygonite, although it differs in the relative proportions of its constituent elements and in its mineralogical and optical properties. The author is engaged in investigating its precise crystallographic form; up to the present, however, it is uncertain whether the new mineral belongs to the monoclinic or to the triclinic system.

A. P.

On a Fossil Resin, perhaps related to the Amber-producing Flora. By H. Spirgatis.†

A report seems for a long time to have been current among the collectors of amber on the sea-coast of Eastern Prussia, that this substance is sometimes met with in a soft "unripe" condition. No specimen, however, could be procured for a long time, until in the last summer a piece of the substance in question, about half the size of a fist, was brought up from the bottom of the Baltic, not far from Brüsterort, in East Prussia.

* Compt. rend., lxxiv, 306. † N. Repert. Pharm., xx, 321.

It consisted of an interior almost transparent yellowish portion, surrounded by a thin opaque crust. The interior portion in the fresh state is soft and somewhat elastic; by exposure to the air it becomes harder and loses its elasticity. Its specific gravity is 0·934. It is nearly insoluble in caustic alkalis, alcohol, and oil of turpentine; it swells in chloroform, carbon disulphide, and petroleum, but does not dissolve in them.

Exposed for some time to 100° it darkens in colour and increases in weight, in consequence of absorption of oxygen; it begins to melt at 300°, and decomposes at a still higher temperature.

Succinic acid was not detected either in the ethereal extract of the resin or among the products of its distillation. The resin is free from sulphur, but contains a small quantity of nitrogen. No separation of the substances constituting the resin could be effected, owing to lack of material. Analysis showed that it contained 86·02 per cent. carbon, 10·93 per cent. hydrogen, deducting ash, of which the substance contained 0·33 per cent. These numbers differ very considerably from those which Schrötter obtained for pure amber: 78·6 per cent. carbon, 10·19 per cent. hydrogen, allowance being made for ash.

The Brüsterort resin has very great similarity to a substance called krantzite, which occurs in the lignite of Lattorf. It agrees also in percentage composition with the asphalte of Bentheim, with a fossil resin from the East Indies analysed by Duflos, and with another examined by Johnston.

W. H. D.

On the Hydrozincite of Auronzo. By A. Cossa.*

This mineral originally found at Bleiberg in Corinthia, and analysed by Smithson in 1803 (called zinc-bloom by Rammelsberg, and zinconise by Beudant), occurs also as a white earthy coating on the deposits of calamine associated with galena in the Argentiera Mine, situated in the commune of Auronzo, in the extreme northern limit of the Cadore. This earthy deposit was found by the author to contain 14·55 p. c. CO_2, 73·21 ZnO, and 11·83 H_2O, answering to the formula—

$$ZnO.3CO_2 + 3aq., \text{ or } 3ZnCO_3.ZnH_2O_2 + 2aq.,$$

and not differing greatly in composition from the hydrozincites hitherto examined.†

* Gazzetta chimica Italiana, i, 43.

† These, according to the analyses given in Rammelsberg's Mineralchemie (p. 239), contain from 12·1 to 15·0 p.c. CO_2, 71·4 to 75·2 ZnO, and 11·2 to 15·1 water. They appear to be mixtures of zinc carbonate and zinc hydrate in various proportions.

For the understanding of the formation and decomposition of minerals, it is important to ascertain the intensity of the solvent action exerted upon them by water saturated with carbonic acid. In this respect the carbonates of zinc, native and artificial, exhibit considerable diversities, as the following table will show:—

	Quantity of material dissolved by 1000 parts by weight of water saturated with CO_2.	Temp.	Pressure.
Hydrozincite of Auronzo	0·355	18°	758 mm.
Basic zinc carbonate precipitated in the cold.....	0·742	17°	759 ,,
Smithsonite ($ZnCO_3$) from Tarnowitz, in well-defined crystals	0·367	18°	753 ,,
Smithsonite from Moresnet, perfectly crystallised....	0·435	14°	757 ,,
Stalactitic calamine from Domos novos (Iglesias)..	0·850	15°	749 ,,

Basic zinc carbonate obtained by precipitation, perfectly washed and dried at 100°, was found by the author to contain 14·18 p. c. CO_2, 64·89 ZnO., and 20·15 water. The Smithsonites of Tarnowitz and Moresnet consist of very pure normal zinc carbonate. The calamine of Iglesias gave by analysis—

H_2O and CO_2.	SiO_2,	ZnO.	FeO.	CuO.	PbO.
12·20	23·07	58·64	3·88	0·45	trace = 98·24

The solution of this mineral in carbonic acid water contained—besides zinc carbonate—silica, ferrous oxide, and a trace of copper oxide.

The carbonic solution of the hydrozincite of Auronzo, yielded by spontaneous evaporation a crystalline powder containing 12·98 p. c. CO_2, 71·25 ZnO., and 15·16 H_2O., which may be represented by the formula $4ZnO.3CO_2 + 4aq$, identical with that of the hydrozincite from Bleiberg, analysed by Smithson.

H. W.

Organic Chemistry.

New Modes of Formation of Hydrocarbons. By Fr. Pfankuch.*
Preliminary notice.

The author has previously shown that potassium phenate and potassium benzoate yield, when heated together, potassium carbonate and diphenyl. Similarly, he now finds that potassium phenate distilled with potassium acetate yields methylbenzene (toluene); and that potassium ethylate distilled with potassium benzoate furnishes ethylbenzene, the yield in both cases being small, in consequence of carbonisation. The addition of pumice or fine sand, and employment of an excess of the acid salt was found advisable. On distilling a mixture of potassium phenate and succinate, a distillate was obtained, yielding, on addition of soda, an oil separable by rectification into toluene and a portion which exhibits a tendency to crystallise and has a highly unpleasant smell; its nature has not yet been determined. Potassium phenate and oxalate yield diphenyl, readily obtained pure by washing with soda, then dissolving in alcohol, and precipitating with water. Mononitrodiphenyl forms the product of the distillation of a mixture of potassium phenate and nitrobenzoate.

The author has also instituted experiments on the action of sulphur on the salts (chiefly barium) of organic acids. On heating barium benzoate, and sulphur, there is obtained, besides benzene, a crystalline product in considerable quantity, which, under the microscope, is seen to consist principally of two different bodies. The greater portion is tolane, $C_{14}H_{10}$, mixed with sulphotolane. To obtain this pure, the mixed product is distilled either over finely divided lead, obtained from lead acetate by precipitation with zinc, &c., or by heating in ethereal solution in sealed tubes with lead or copper, and subsequent fractional distillation. Reaction takes place in the main according to the equation:—

$$(C_6H_5COO)_2Ba + S = SO_4Ba + (C_7H_5)_2.$$

The separation of the products obtained by heating barium acetate and sulphur together is not so readily accomplished, but the author is certain that he has obtained the hydrocarbons, C_4H_6, in a pure state, as one of them.

H. E. A.

* J. pr. Chem. [2], iv, 35.

Researches on the Hydrocarbons of the Series C_nH_{2n+2}.—No. VII. By C. SCHORLEMMER.

THE following *normal* paraffins* have been investigated by the author:—

	From petroleum.	From the acids of the series $C_nH_{2n-2}O_4$.	So-called alcohol-radicals.	
C_5H_{12}..	37°— 39°	—	—	
			Dipropyl.	From mannite.
C_6H_{14}..	69°— 70°	69·5°	69°—70°	71·5°
C_7H_{16}..	98°— 99°	100·5°	—	—
			Dibutyl.	From methyl-hexyl carbinol.
C_8H_{18}..	123°—124°	123°—124°	123°—124°	124°

That these paraffins have really the constitution ascribed to them follows partly from their mode of formation; thus dipropyl was obtained from normal propyl iodide, and dibutyl from normal butyl iodide. The constitution of the others was determined by converting them into alcohols and studying the oxidation products of the latter; thus the hexyl hydride from petroleum, as well as that obtained from mannite, was transformed into secondary hexyl alcohol, which on oxidation yielded acetic acid and *normal* butyric acid.

The hydrocarbon C_8H_{18} obtained from methyl-hexyl carbinol is identical with dibutyl and with the hydrocarbon which Zinke obtained from primary octyl alcohol. This chemist prepared also dioctyl, $C_{16}H_{34}$, which consequently is also a normal paraffin; and it appears probable that dihexyl, which Brazier and Gosleth obtained by the electrolysis of œnanthylic acid, belongs also to this group.

We are now acquainted with the following normal paraffins:—

	Boiling points.		
	Found (mean).	Calculated.	Difference.
$C\ H_4$	—	—	
$C_2\ H_6$	—	—	
$C_3\ H_8$	—	—	
$C_4\ H_{10}$	1°	1°	
$C_5\ H_{12}$	38°	38°	37°
$C_6\ H_{14}$	70°	71°	33°
$C_7\ H_{16}$	99°	100°	29°
$C_8\ H_{18}$	124°	125°	25°
$C_{12}H_{26}$	202°	201°	4 × 19°
$C_{16}H_{34}$	278°	278°	4 × 19°

* See Proc. Roy. Soc., xvi, 367.

From this it appears that the boiling-point is not raised 31° for each addition of CH_2, as formerly assumed, but that, as the calculated numbers show, the difference between the boiling-points of the lower members decreases regularly by 4°, until it becomes the well-known difference of 19°.

C. S.

Syntheses by means of Nascent Formic Acid. By CARSTANJEN and SCHERTEL.*

If formic acid be capable of directly uniting with non-saturated hydrocarbons, &c., acids should be formed containing more carbon than the hydrocarbon employed, *e.g.*, ethylene should yield propionic acid. A rapid stream of ethylene was passed through a boiling mixture of 25 grm. KCy, 50 grm. KHO, and 250 parts H_2O; the issuing gas was passed through hydrochloric acid, almost the whole of the ethylene used being absorbed; by evaporation of the hydrochloric acid, and extraction with absolute alcohol, a platinum salt was ultimately obtained, containing 41 per cent. of platinum; the ethylamine salt would require 39·7, and the ammonia salt 44·4 per cent.

The contents of the flask in which the reaction took place were distilled with sulphuric acid, and the distillate was converted into lead salt, but little of which was soluble. When the soluble portion was distilled with sulphuric acid, the distillate boiled with mercury oxide to remove formic acid, the product treated with hydric sulphide, and the filtrate with silver carbonate, a small quantity of the characteristic needles of silver propionate was obtained, but not enough for analysis.

Ethylene was passed through a mixture of oxalic acid and glycerin at 110°—120°; after distillation with water and treatment as above described, small quantities of crystalline silver salt were obtained.

Attempts to synthesise acids by the action of nascent formic acid produced by the action of hydrochloric and hydrocyanic acids, and to unite formic acid with nascent ethylene, are contemplated; also to unite formic acid with the unsaturated acids, such as fumaric, maleic, itaconic, &c.

C. R. A. W.

A New Theory of Fermentation. By A. PETIT.†

An attentive study of the phenomena of fermentation has led the author to propose a new theory, based on the following facts:—

1. Ferment globules may be produced without fermentation.

2. Fermentation may take place, as has also been shown by Berthelot, in the absence of ferment globules.

* J. pr. Chem. [2], iv, 51. † Compt. rend., lxxiii, 267—270.

3. In a filtered fermentable liquid, globules form without inducing fermentation. It commences only when a certain number of globules are deposited at the bottom of the vessel, the bubbles of carbonic anhydride then proceeding exclusively from the bottom.

4. Fermentation is retarded, and even stopped, when the sugar is in very dilute solution.

5. By augmenting the relative proportion of ferment, the resistance which certain anti-fermentescible substances, creosote, sublimate, organic and mineral acids, oppose to fermentation may be overcome.

6. When the proportions of ferment and sugar are suitable, fermentation commences instantaneously.

7. By varying the sugar within very wide limits (from 20—300 grms. per litre in the author's experiments), the volume of gas disengaged is the same for the same quantity of ferment.

8. After a certain time, necessary to attain a maximum, the quantity of gas disengaged is exactly proportional to the time.

9. Sulphites do not prevent fermentation; they are converted into sulphates.

10. Beer-yeast suspended in water absorbs a certain quantity of iodine, converting it into hydriodic acid. This liquid saturated with iodine can, after fermenting some time, again absorb a further quantity. In presence of yeast, water is thus decomposed, the hydrogen uniting with the iodine, the oxygen with the globules. This property of the globules of absorbing oxygen has, moreover, been thoroughly established in the case of the blood-corpuscles and the acetous ferment.

On these observations the following theory is founded. The sugar being dissolved in water in presence of yeast, water becomes decomposed, and hydrogen and oxygen are set free. The oxygen enters, momentarily at least, into combination with the substance of the globules; the hydrogen in the nascent state attaches itself to a molecule of sugar, and causes its decomposition, the products being alcohol, carbonic anhydride, and one equivalent of hydrogen, which decomposes a further molecule of sugar, and so the reaction proceeds:—

$$C_6H_{12}O_6 + H = 2C_2H_6O + 2CO_2 + H.$$

A single molecule of hydrogen should theoretically decompose an indefinite quantity of sugar, were it not that secondary reactions occur, the principal of which consists in the formation of glycerin:—

$$C_6H_{12}O_6 + 4H = 2C_3H_8O_3.$$

The author was led to consider the hydrogen the prime agent—although the oxygen may equally well be so regarded, and nothing proves that under certain conditions of experiment it is not so—by the fact that on allowing two similar liquids to ferment, but with the

addition of 1 per cent. of sodium sulphite to the one, the same disengagement of carbonic anhydride took place in both cases, although the oxygen had served to convert the sulphite into sulphate. In this experiment no acids were formed.

If the fermentation takes place in the absence of sulphites, the oxygen forms succinic and acetic acids.

H. E. A.

On the Gases enclosed in Coal. By ERNST VON MEYER.*
Preliminary notice.

THE author has examined the gases enclosed in Zwickau coal. Pieces, the size of a nut, of a hard, dense coal were introduced into a flask filled with recently boiled hot water, and a caoutchouc stopper and bent tube afterwards inserted into the neck. The water was first allowed to boil for some time, in order to remove the greater part of the air mechanically adhering to the coal, and the gases were then collected in a tube filled with boiled water, and subsequently analysed by Bunsen's method. The following are the percentage compositions of two such portions of gas :—

	I.	II.
Carbonic anhydride	16·9	22·4
Marsh gas	20·4	22·3
Nitrogen	53·3	48·0
Oxygen	1·7	4·1
Heavy hydrocarbons absorbed by sulphuric acid	7·7	3·2
	100·0	100·0

The large amount of nitrogen and small amount of oxygen is noteworthy, the latter having doubtless been expended in oxidation. The coal examined had lain for some months in a cellar in contact with the atmosphere. Remarkable is the amount of heavy hydrocarbons present in the gas; and since it is conceivable, although improbable, that these were first formed on heating the coal under water to 100°, the author proposes to submit the gases extracted by means of a mercury pump to examination, and also to extend his investigation to various sorts of coal.

H. E. A.

* J. pr. Chem. [2], iv, 42.

New Derivatives from Carbon Chloride. By H. HOCH and H. KOLBE.*

NITROGEN tetroxide combines directly with carbon dichloride, forming a crystalline body, $C_2Cl_4(NO_2)_2$. Attempts to reduce this to the corresponding amido-compound have been as yet fruitless.

Strong alcoholic potash-ley acts violently on this substance; if water be added to strong alcoholic potash, and this dinitrocarbon chloride gradually added to the mixture, the formation of bye-products may be avoided; an alkaline liquid is obtained, which by evaporation yields two sets of crystals, viz., potassium chloride, and long prisms, which agree in composition with the formula, $\left.\begin{matrix}CCl_3\\NO_2\\NO_2\end{matrix}\right\}C.OK$. This may be regarded as the potassium salt of trichloracetic acid in which the oxygen of the group CO is replaced by two atoms of nitryl; or it may be viewed as trichloro-dinitro-ethyl alcohol.

Carbon chloride (? sesquichloride) and alcoholic potash furnish a crystalline soluble potassium salt, which has probably the formula $\left.\begin{matrix}CCl_3\\Cl_2\end{matrix}\right\}C.OK$.

C. R. A. W.

Attempts to Prepare Carbonyl Cyanide $CO(CN)_2$. By CARSTANJEN and SCHERTEL.†

No carbonyl cyanide is found by heating mercury cyanide in carbon oxide, and passing the resulting gases through a cold U-tube.

Carbon oxide does not unite in sunlight with cyanogen. Attempts to prepare the desired body by the action of liquid phosgene on silver cyanide, are in progress.

C. R. A. W.

On the Action of Potassium Sulphydrate on Benzoyl Chloride. By A. WEDDIGE.‡

AN alcoholic solution of potassium sulphydrate produces, by its action on benzoyl chloride, not thiobenzoic acid, as might be expected, but principally a body indifferent to alkalies, and crystallisable from alcohol in pale red needles; this appears from its properties and composition to be identical with the benzoyl sulphide of Liebig and Wöhler.

C. R. A. W.

* J. pr. Chem. [2], iv, 60. † J. pr. Chem. [2], iv, 49.
‡ J. pr. Chem. [2], iv, 59.

On Sulphoform and Cyanoform. By FR. PFANKUCH.*
Preliminary notice.

IODOFORM was heated with sulphur in sealed tubes at a temperature not above the melting point of the latter. After treating the red-brown fused product, first with boiling water to which a little sodium carbonate or hydrate was added, and then, in order to remove the excess of iodoform, repeatedly with ether, a slightly yellow, solid mass remained, readily soluble in carbon bisulphide, and crystallising therefrom most beautifully. A sulphur determination led to the composition $C_2H_2S_3$.

In numerous attempts to obtain cyanoform by heating iodoform with mercuric cyanide in sealed tubes, the author constantly obtained a body which must be regarded as a double salt of cyanoform and mercuric iodide, the analysis yielding numbers agreeing exactly with the formula $2CH(CN)_3.3HgI_2$. This compound forms magnificent glistening needles, which become slightly yellow when exposed to light, and from which water separates the greater part of the mercuric iodide. A detailed description of the products obtainable from this body is promised. The author has succeeded in obtaining cyanoform by Fairley's† method from potassium cyanide and chloroform, although in very small quantities.

H. E. A.

Researches on the Oxidation-products of the Principal Normal Alcohols.
By IS. PIERRE and ED. PUCHOT.‡

THE products of the oxidising action of a mixture of potassium bichromate and sulphuric acid on an alcohol, vary, as is well known, according to the conditions under which the reaction is effected. The principal are: the normal acid corresponding to the alcohol oxidised; its aldehyde; and the compound ether formed by the action of the acid on the alcohol. The vivacity of the reaction, and the nature and relative proportions of the products, may vary considerably according to the relative proportions of alcohol, bichromate, and sulphuric acid; according to the manner of employing them; and according to the quantity of water used to facilitate and regulate the reaction. The authors have studied, and describe in the present memoir, the conditions under which the greatest possible quantity of the compound ether is formed. One of the chief precautions necessary to ensure a satisfactory yield of the ether is the maintenance of the mixture at a low temperature; this is the more advantageous the less

* J. pr. Chem. [2], iv, 38. † Ann. Ch. Pharm. Suppl., iii, 371.
‡ J. Pharm. Chim. [4], xiii, 369—376.

complex the formula and the lower the molecular weight of the alcohol. The authors' experiments further show that the lower the temperature of the mixture is kept during the reaction, all other circumstances being alike, the less is the quantity of aldehyde formed.

The conversion of an alcohol into an ether may be expressed by the following general equation:

$$6C_nH_{2n+1}OH + 2K_2Cr_2O_7 + 8H_2SO_4 = 14H_2O + 3\left\{\begin{matrix} C_nH_{2n+1} \\ COOC_nH_{2n+1} \end{matrix}\right. + 2(K_2SO_4.Cr_23SO_4).$$

Preparation of Amylic Valerate by Oxidation of Amylic Alcohol.—540 grams of amylic alcohol were mixed with 825—850 grams of sulphuric acid, previously diluted with its own volume (about 400 grams) of water and cooled; the whole was poured into a wide-mouthed vessel of 4—5 litres capacity, furnished with a stirrer, and after addition of about 2,250 grams of water, 675 grm. of potassium bichromate in fine powder were gradually introduced in small quantities at a time, the mixture being constantly agitated meanwhile. The vessel containing the mixture was surrounded by cold water, which was frequently renewed. Two such operations were carried on simultaneously, the two vessels being placed side by side, and the stirrer fixed and worked by means of a cord and pulley.

About two hours were required for the introduction of the bichromate. At the termination of the reaction, the liquid being cold, the supernatant layer was removed by means of a tap-funnel, and fractionally distilled. It formed from 84 to 85 per cent. of the weight of alcohol employed, and consisted chiefly (about $\frac{4}{5}$) of amylic valerate, together with amylic aldehyde and a small quantity of unattacked alcohol. The pure amylic valerate thus obtained is a limpid, colourless liquid, of an agreeable fruity odour, boiling constantly at 190°.

	0°	50·67°	100°	149·5°
Specific gravity	·874	·832	·787	·740

From these numbers the authors calculate the specific gravity, and the relative volumes referred to the volume at 0° and to the volume at the boiling point, for every 20 degrees from 0° to 190°.

Preparation of Butylic Butyrate.—A mixture of 340 grams of butylic alcohol and 540 grams of sulphuric acid diluted with 1,500—1,600 grams of water, and previously cooled, was placed in each of the above vessels, which were surrounded by a refrigerating mixture, and 400 grams of bichromate in fine powder were then added to each as before. The mixture was allowed to stand half an hour, and the ethereal layer then separated; this formed from 87 to 88 per cent. of the weight of alcohol employed (the mean of ten double experiments), and consisted mainly of butylic butyrate, with butylic aldehyde and a small quantity

of unattacked alcohol. From this mixture pure butylic butyrate was separated by repeated rectification, as a limpid, colourless liquid, having an agreeable fruity odour, and boiling constantly at 149·5° under a pressure of 758 mm.

	0°	51·8°	99·6°	128·3°
Specific gravity ..	·872	·8245	·776	·7445

From these data is calculated a table of the specific gravities and volumes, and also the rate of contraction for every 20°, taking as starting point and unit of comparison, the volume at the boiling point.

Preparation of Propylic Propionate.—A mixture of 540 grams of sulphuric acid and 1,500 grams of water was introduced, together with 245 grams of propylic alcohol, into each of the vessels, which were surrounded by a refrigerating mixture; 370 grams of bichromate were then gradually added to each, the operation lasting about three hours. In order to obtain a good yield of ether, it is especially necessary, in this instance, that the operation be conducted slowly and the mixture maintained at a low temperature. The product is principally propylic propionate, containing a little propylic aldehyde and a small quantity of unattacked alcohol. The yield of crude product was from 75 to 76 per cent. of the weight of alcohol employed. The liquid remaining after the separation of the ether still contains in solution a small quantity of ether, as well as a notable proportion of propionic acid; these may be recovered by distillation. The pure ether, obtained by rectification, a colourless limpid liquid boiling at 124·3°, was compared with the ether prepared by the action of a mixture of sulphuric acid and propylic alcohol on potassium propionate and found identical therewith.

	0°	51·27°	100·6°	108·34°
Specific gravity	·903	·857	·797	·785

[Here follows a table, calculated from the above data, of the specific gravities and volumes for every 20°.]

H. E. A.

On the Action of Ethylene Iodide on Acetylide of Copper. By E. Carstanjen and A. Schertel.*

This reaction was investigated in the hope of obtaining a hydrocarbon, C_6H_6, isomeric with benzene:

$$C_2H_4I_2 + C_4H_2Cu = C_6H_6 + CuI_2.$$

Acetylide of copper suspended in ether was heated in sealed tubes with a slight excess of ethylene iodide to 85°—95°, a temperature at

* J. pr. Chem. [2], iv, 47.

which the latter when heated alone is resolved into ethylene and iodine. The action seems to be complete at the end of about 5—6 hours, when the red colour of the acetylide having disappeared, the tube contains a grey-green mass of copper iodide and a clear liquid. On opening the tubes, considerable quantities of gas burning with a luminous flame escaped. The ethereal solution left on evaporation a body crystallising in beautiful broad prisms concentrically grouped, which, when recrystallised from hot alcohol, forms pale yellow glistening prisms. The new compound exhibits a remarkable stability: it volatilises when quickly heated in the form of white vapours, without previously melting, and without the least decomposition. A mixture of concentrated nitric and sulphuric acid seems to be without action in the cold; but it is soluble in the latter on heating, forming a colourless liquid. It contains iodine, and evolves when heated with lime an intense alliaceous odour, perfectly different from that of acetylene. It has not yet been analysed, so that it is undetermined whether the oxygen contained in acetylide of copper has taken part in the reaction or not; if so, the authors propose to act on ethylene iodide with allylene silver, C_3H_3Ag, which according to Liebermann certainly contains no oxygen.

H. E. A.

On Ethyl Sulphides. By M. Müller.*

(Preliminary notice.)

Mercaptan, when heated in a sealed tube for six hours, to 150°, with sulphur in the proportion of 2 molecules to 1 atom of the latter, is decomposed according to the equation—

$$2C_2H_5SHS + S = (C_2H_5)_2\ S + H_2S.$$

Selenium is without action on mercaptan. Ethyl sulphide, $(C_2H_5)_2S$, is entirely unacted on by sulphur, and, when mixed with mercaptan, may be readily obtained pure, by heating with the mixture sulphur, whereby the mercaptan is converted into ethyl sulphide and hydrogen sulphide.

Ethyl disulphide, $(C_2H_5)_2S_2$, heated with sulphur yields a yellow coloured oil, heavier than water, which cannot be distilled unchanged, but may be obtained pure by slowly distilling it in a current of steam; this is ethyl trisulphide, $(C_2H_5)_2S_3$. To obtain this body, liver of sulphur and potassium sulphovinate are distilled from a retort, with frequent addition of water, so long as oily drops pass over. The oil thus obtained is a mixture of ethyl di- and tri-sulphides, and to convert it entirely into the latter, it is heated with sulphur in sealed tubes for some hours at 150°. The contents of the tubes are then carefully dis-

* J. pr. Chem. [2], iv, 39.

tilled in a current of steam, and this product may be looked upon as pure.

On shaking *ethyl trisulphide* with mercury, the third sulphur-atom is slowly removed; also on heating with copper turnings in a sealed tube to 150° for a day. When the product is suspended in water and carefully oxidised by fuming nitric acid, an amount of sulphuric acid is produced exactly equivalent to the third sulphur-atom, two molecules of ethylsulphonic acid being formed at the same time. The above-mentioned mixture of di- and tri-sulphides may therefore be employed with advantage for the preparation of ethyl sulphonic acid, $C_2H_5SO_2OH$. On continued shaking, aqueous potash removes the third sulphur-atom. Alcoholic potash seems to act differently; heated with potassium cyanide it yields potassium sulphocyanate and ethyl disulphide. Many metallic salts remove the third sulphur atom, with simultaneous formation of metallic sulphide. Silver oxide forms silver sulphide and ethylsulphonic acid; silver acetate acts similarly, acetic acid being set free. From these experiments it might be concluded that the third sulphur atom in ethyl trisulphide is held very loosely; this, however, does not seem to be the case under all circumstances. It might thus be expected that the equation:

$$(C_2H_5)_2S + 2(C_2H_5)HS = 2(C_2H_5)_2S_2 + H_2S,$$

should be realisable. No such reaction, however, takes place, even after heating for three days at 150°.

H. E. A.

On the Atomic Volume of Allyl Alcohol. By H. L. Buff.*

Buff criticises Tollens's determination of the atomic volume of allyl alcohol on grounds which affect the use of Kopp's numbers in some cases. Tollens's determination agreed with the volume calculated by using Kopp's values for carbon, hydrogen, and oxygen. But Buff observes that differences exist between these calculated numbers and the numbers actually obtained for compounds which contain bivalent carbon atoms. Of such are allyl derivatives. Buff found the atomic volume of diallyl to be 126·7—127·0; calculated by Kopp's numbers it is 121.

From numerous determinations he finds the atomic volume of an allyl alcohol which boiled at 96·5°—96·8° to be 74·6° and at 96·5° somewhat greater than that which is commonly given as the result of calculation. The real number would be higher than 74·6°, as the alcohol still contained a little water, which is very difficult to separate, and tends to lower the atomic volume. This is shown by the fact that

* Deut. Chem. Ges. Ber., iv, 647.

an allyl alcohol which contained water, and boiled at 93°, had at that temperature an atomic volume of 72·3.

W. H. D.

On the Relations between Glycerin and Allyl Compounds. By H. HUEBNER and K. MUELLER.*

THE dichlorhydrin prepared by Berthelot's method by passing dry hydrochloric acid gas into a mixture of glacial acetic acid and glycerin, is a mixture of two isomerides. One of these, boiling at 174°, is obtained in the pure state by combining epichlorhydrin with hydrochloric acid; the other, which boils at 182°, is identical with dichlorallyl alcohol, which compound is best prepared by passing dry chlorine over anhydrous allyl alcohol.

Both compounds, when acted upon by sodium in presence of ether, yield allyl alcohol, and both are converted into epichlorhydrin by the action of alkalis.

When dry epichlorhydrin is added, drop by drop, to sodium, in presence of anhydrous ether, a brisk reaction sets in. The white powder which is formed is soluble in water. On evaporating to dryness, exhausting the residue with absolute alcohol, and evaporating this solution, a syrupy liquid is left behind, which distils with partial decomposition at 218°—225°. It has the composition $C_6O_{12}H_2$, and appears to be a kind of polymeric allyl alcohol, formed thus:—

$$2\left\{\begin{matrix} CH_2 \\ CH \\ CH_2Cl \end{matrix}\right\}O + 2Na_2 = \begin{matrix} CH_2 & \text{———} & CH_2 \\ | & & | \\ CH.ONa & & CH.ONa \\ | & & | \\ CH_2 & \text{———} & CH_2 \end{matrix} + 2NaCl.$$

By acting with water on the sodium-compound, the sodium is replaced by hydrogen.

C. S.

Observations on the Allyl Group. By A. OPPENHEIM.†

TRICHLORALLYL is only with the greatest difficulty acted upon by chlorine. On dissolving iodine in the trichlorallyl, and passing dry chlorine into the heated liquid, whilst exposed to sunlight, a small quantity of white crystals gradually separated, which were found to be *perchlorethane*, C_2Cl_6. The action of chlorine on trichlorallyl consists, therefore, of a destruction of the molecule. A similar observation has been made by Beilstein, who, by continued action of chlorine upon toluene, obtained derivatives of benzene.

* Ann. Ch. Pharm., clix, 168—188. † Deut. Chem. Ges. Ber., iv, 669—672.

Mercury-allyl iodide, C_3H_5HgI, is best obtained by shaking mercury with a mixture of equal volumes of allyl iodide and alcohol. It crystallises from carbon disulphide and acetone in white scales, which soon turn yellow. It is not acted upon either by phosphorus tribromide or by acetyl chloride or benzoyl chloride. On adding it to a solution of zinc-ethyl in ether, an energetic reaction sets in, the products being mercury, zinc iodide, mercury-ethyl, and diallyl:

$$2C_3H_5HgI + Zn(C_2H_5)_2 = Hg + Hg(C_2H_5)_2 + ZnI_2 + (C_3H_5)_2.$$

A solution of potassium cyanide acts on mercury-allyl iodide quickly in the cold, according to the equation—

$$2C_3H_5HgI + 2KCN = Hg + 2KI + Hg(CN)_2 + (C_3H_5)_2.$$

Besides these products, two mercury-allyl compounds are probably formed, one of which is liquid, and explodes when the distillation of the diallyl is not stopped in time.

The mercury compounds of allyl attack the skin, but the action becomes perceptible only after 6—8 hours, when painful blisters appear.

C. S.

Miscellaneous Notes. By L. Henry.*

1. *On the Isomerism of Glycerin Derivatives having the formula* $C_3H_5X_3$.—Discusses the constitution of these bodies, which may be derived either from glycerin or from allyl compounds.

2. *On some Derivatives of Glycerin.—Dichloriodohydrin*, $C_3H_5Cl_2I$, obtained by acting on chloriodohydrin with phosphorus pentachloride, is a colourless liquid, with a faint ethereal smell, boiling at 205°. It is neutral, but soon becomes acid when in the moist state.

Chlorobromiodohydrin, C_3H_5ClBrI, obtained by acting with phosphorus pentabromide on chloriodohydrin, is a substance with similar properties, but decomposed on boiling, free iodine and acid vapours being given off.

Chlorbromonitrin, $C_3H_5ClBr(NO_3)$, formed by adding chlorbromohydrin in small quantities to a mixture of nitric and sulphuric acids, is a thick colourless liquid, having a pungent smell and a bitter and acid taste.

Glyceryl Chloronitrosulphate, $C_3H_5Cl(NO_3)(SO_4H)$, is a thick sticky liquid, insoluble in water, which is obtained by treating glyceryl chlorosulphate with fuming nitric acid, or by acting on epichlorhydrin with a mixture of nitric and sulphuric acids.

Dichloracetin, $C_3H_5Cl_2(C_2H_3O_2)$, a colourless neutral liquid, with a

* Deut. Chem. Ges. Ber., iv, 701—707.

refreshing smell, and boiling at 194°—195°, is formed by heating dichlorhydrin with acetyl chloride.

Bromodiethylin, $C_3H_5Br(OC_2H_5)_2$, formed by acting with phosphorus pentabromide on diethylin, is a yellowish liquid, with a pungent smell, boiling at about 200°.

3. *Preparation of Dichlorhydrin.*—The author describes the method he employs to prepare this compound in large quantities, according to the method of Berthelot and Reboul.

4. *Ethyl Glycerate*, $C_3H_3O(OH)_2(OC_2H_5)$.—This compound, which Debus did not succeed in obtaining, can be prepared by heating concentrated glyceric acid with 3—4 vol. of absolute alcohol for some hours to 170°—190°. It is a thick, sticky, colourless liquid, which boils at 230°—240°, and has a bitter taste. On treating it with a mixture of nitric and sulphuric acids, the compound $C_3H_3O(OC_2H_5)(NO_3)_2$ is obtained, as a heavy colourless oil.

5. *Diethyl Glycollate*, $C_2H_3O_3(C_2H_5)_2$.—This compound, which, according to Heintz, is but slowly formed by heating sodium-ethyl glycollate with ethyl iodide, can be easily obtained by gradually adding a solution of sodium ethylate in absolute alcohol to ethyl monochloracetate, heating the mixture for some time, and isolating the ether by fractional distillation.

C. S.

Action of Sodium Amalgam on Oxalic Ether. By S. FRIEDLAENDER.*

A. EGHIS obtained by this reaction *glycollic acid* and not *glycollinic acid.*† This is not surprising, as the products may differ according to the time of the reaction and probably also according to the temperature. But as Eghis seems to doubt the existence of glycollinic acid, the author replies that the acid which he obtained could in no case be glycollic acid, for the following reasons:—

Glycollinic acid crystallises with $4\frac{1}{2}$ H_2O and is amorphous in the anhydrous state. Calcium glycollate contains 3 per cent. more calcium than the glycollinate, and only 27·48 per cent. H_2O, whilst the glycollinate contains 53·16 per cent. Copper glycollate crystallises without water, and the glycollinate with 22·68 per cent. The crystallised silver glycollinate is anhydrous, whilst the glycollate crystallises with 4·3 per cent. of water. Now as the results of the analysis agree closely with the calculated composition, there can be no doubt that the two acids are different compounds.

C. S.

* Deut. Chem. Ges. Ber., iv, 710—711. † Page 820 of this volume,

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Contributions to our Knowledge of the Benzylic Ethers. By F. SINTENIS.*

ON treating these ethers with chlorine or bromine, no substitution-products are formed, but the compounds are decomposed. Benzyl-methyl ether and benzyl-ethyl ether, when acted upon by dry chlorine in the cold, yield oil of bitter almonds, hydrochloric acid and methyl—or ethyl-chloride; and chlorobenzyl ethylether is decomposed into chlorobenzoic aldehyde and ethyl-chloride. By the action of chlorine at the boiling point, the methyl and ethyl ethers yield methyl or ethyl chloride and benzoyl chloride, and the chlorbenzyl ethylether splits up into chlorobenzoyl chloride and ethylchloride. When benzoyl-ethyl ether is acted upon by chlorine in presence of iodine, the products are ethyl iodide and monochlorbenzoyl chloride, which by oxidation is converted into parachlorobenzoic acid.

Benzyl-phenyl ether,† which contains two benzene residues, is also decomposed by chlorine or bromine, which when acting in the cold yield trichlorophenol or tribromophenol and benzyl chloride or bromide. As a similar decomposition takes place when only one molecule of chlorine or bromine is used, it is obvious that in the first stage of the reaction a substituted ether is formed, which is further decomposed by the hydracid produced, just as the anisols are split up by the action of hydriodic acid; and indeed by heating benzyl-phenyl ether with hydrochloric acid to 100°, benzyl chloride and phenol were formed.

To obtain substitution-products, it is therefore necessary to remove the acid, as soon as it is formed, which is easily effected by adding mercuric oxide. By adding bromine to an alcoholic solution of the ether, in which freshly precipitated mercuric oxide was suspended, benzyl-bromophenyl ether, $C_6H_5.CH_2OC_6H_4Br$, was formed. This compound crystallises from alcohol in long white needles, melting at 59°—59·5°; it is not acted upon by caustic soda-solution. By the action of chlorine under the same conditions, the chlorinated ether, $C_6H_5.CH_2OC_6H_4Cl$, was obtained, which forms long needles melting at 71°—71·5°.

C. S.

* Deut. Chem. Ges. Ber., iv, 697—700.

† This ether was prepared by heating an alcoholic solution of benzyl chloride and potassium phenate. After the decomposition was complete, the alcohol was distilled off, and steam passed through the residue, to remove small quantities of benzyl chloride and phenol. The ether left behind was washed with water, and crystallised from alcohol; it melts at 38°—39°, and boils at 286°—287°.

On Phenol Colours. By A. BAEYER.*

FURTHER researches on the formation of gallein and fluorescein† have shown that the phthalic acid not only acts by abstracting water, but that it enters the molecule of the new compounds. All phenols are acted upon by heating them, not only with phthalic acid, but also with other polybasic organic acids, and with aldehydes, either alone or with the addition of sulphuric acid or glycerin. The compounds thus formed are not ethers; some are indifferent bodies; others dissolve in potash with an intense colour which disappears on reduction. Those which give coloured solutions yield, when heated with sulphuric acid, new coloured bodies, differing from the former in yielding coloured reduction products. Of the almost unlimited number of new compounds which can be obtained by this method, the following were prepared by the author and his pupils.

Phenol Colours.—On heating a mixture of 10 parts of phenol, 5 parts phthalic anhydride and 4 parts of concentrated sulphuric acid for some hours to 120°—130° a red mass is obtained, which, when treated with boiling benzene, is converted into a yellowish white powder. It dissolves in caustic potash with a splendid magenta colour; hydrochloric acid precipitates it from this solution in white resinous flakes. The *phthalein of phenol* has the composition $C_{20}H_{14}O_4$, and is formed according to the equation—

$$C_8H_4O_3 + 2C_6H_6O = C_{20}H_{14}O_4 + H_2O.$$

On heating the alkaline solution with zinc-dust, it becomes colourless, and by adding hydrochloric acid the *phthalin of phenol*, $C_{20}H_{16}O_4$, is obtained as a white granular precipitate.

Mellitic and pyromellitic acid act similarly to phthalic acid; but most interesting is the action of oxalic acid on phenol, by which rosolic acid is formed. Dale and Schorlemmer have lately isolated from the crude rosolic acid the pure aurin, to which they have ascribed the formula $C_{21}H_{18}O_3$; but it appears more probable that the true formula is $C_{25}H_{18}O_3$, with which the results of the analysis also agree well; because it seems most likely that the elements of oxalic acid take part in the reaction by which leuco-aurin is formed in the first instance,

$$CO_2 + 4C_6H_6O = C_{25}H_{20}O_4 + 2H_2O.$$

which by subsequent oxidation is partly converted into aurine; this is the more probable, as the numbers which Kolbe and Schmitt obtained by analysing crude rosolic acid, come nearer to the composition of leuco-aurin than to that of aurin.‡

* Deut. Chem. Ges. Ber., iv, 658—665. † Page 834 of this volume.

‡ *Note by the Abstractor.*—Crude rosolic acid contains a very large quantity indeed

α-Naphthol Colours. By J. Grabowsky. — When naphthol and phthalic anhydride are boiled together, water is given off, and the liquid assumes a dark green colour. On exhausting the cooled mass with alcohol, a white substance is left behind, which crystallises from hot benzene in splendid shining yellowish crystals. It is insoluble in aqueous potash; by heating it with an alcoholic potash-solution, it is converted into a green body. The white substance is formed according to the equation—

$$C_8H_4O_3 + 2C_{10}H_8O = C_{28}H_{16}O_3 + 2H_2O.$$

It contains one molecule of water less than the naphthol ether of phthalic acid and the isomeric phthalein of naphthol, and may be called the anhydride of the latter compound. On heating it with sulphuric acid, it yields a red body, which is no colouring matter, and has great resemblance to Laurent's carminaphte.

On heating naphthol with oxalic and sulphuric acid to 120°—130°, a green body soluble in potash is formed, besides a white indifferent substance, which appears to be a mixture of different bodies. Mellitic and pyromellitic acid yield, when gently heated, substances which dissolve in potash with a green colour; but on stronger heating white indifferent compounds are formed. Phthalic chloride produces at 100°, besides an indifferent body, one dissolving in potash with a green and another with a blue colour.

Resorcin Colours.—The *phthalein of resorcin*, or *fluorescein*, $C_{20}H_{12}O_5$, is obtained by heating resorcin and phthalic anhydride to 195°. It crystallises from alcohol in brown crusts; from the alkaline solution acids precipitate it as a brick-red powder; by treating it with zinc-dust in an alkaline solution, it is reduced to colourless phthalin. On heating it strongly with sulphuric acid, a red body is formed, which dissolves in alkalis with a blue colour; on adding zinc-dust to this solution, it changes into red. This red solution dyes blue like indigo, but the colour is neither fine nor fast.

By acting on resorcin with succinyl chloride, Malin obtained a yellow resin, which has great resemblance to the phthalein just described. The same substance is obtained by using succinic anhydride; it is most likely the succinein of resorcin.

When resorcin is heated with oxalic and sulphuric acids, a yellow compound is obtained, which appears to be a mixture, and probably contains euxanthone, $C_{13}H_8O_4$.

On heating *hydroquinone* with phthalic and sulphuric acids, a red phthalein is formed, which dissolves in potash with a violet colour, and dyes iron and alumina mordants like barwood

of a colourless compound, which D. and S. have not yet obtained in the pure state, but which exhibits some of the reactions of leuco-aurin.

On treating *pyrocatechin* in the same way, and adding water, a green liquid is obtained, which gives with potash a transient blue colour.

Pyrogallic acid Colours.—The true formula for gallein is $C_{20}H_{12}O_7$, and not $C_{18}H_{14}O_7$, as formerly stated. It is formed according to the equation:

$$C_8H_4O_3 + 2C_6H_6O_3 = C_{20}H_{12}O_7 + 2H_2O.$$

It is therefore the *phthalein of pyrogallic acid.* It dissolves in a concentrated solution of pyrogallic acid. By adding water to this solution, a precipitate is obtained which when dried at 100° has the composition $C_{20}H_{12}O_7 + H_2O$. With alcohol it forms a crystalline compound. Gallin has the composition $C_{20}H_{18}O_7$, and cærulein $C_{20}H_{10}O_7$.

Compounds resembling gallein are obtained, as already mentioned, by a great number of other acids, and it appears that oil of bitter almonds, acetone, &c., can also by the same method be combined with pyrogallic acid.

Phloroglucin yields a yellow, and *morin* a red compound, when heated with phthalic anhydride and sulphuric acid.

The constituents of these new compounds may be divided into two groups, the phenols, and the bodies which keep them together, the former being the chromogenous constituents, as the colour is but little changed, if at all, by using different acids, &c. A great number of natural colours, and chiefly those of the different dyewoods, have, no doubt, a similar constitution. The nature of the chromogenous constituents of these colours can in most cases be found by fusion with potash, or by treating with nitric acid; but it will be far more difficult to detect the compounds which connect the chromogenous constituents, as in the natural colours compounds belonging to the sugar group or vegetable acids seem to play this part. Thus hæmatein yields pyrogallic acid on fusion with potash, showing that it is a derivative of either this acid or of hydroquinone or pyrocatechin, which are converted into pyrogallic acid by the action of potash. If the formula for hæmatin is really $C_{16}H_{12}O_6$, the connecting body $C_4H_6O_3$ might be either a derivative of crotonic acid or an aldehyde of succinic acid. C. S.

On the Colouring Matter of Cochineal. By C. Liebermann and W. A. van Dorp.*

In order to get an insight into the constitution of this colouring matter, the authors have investigated the nitrococcusic acid, $C_8H_5(NO_2)_3O_3$, which Warren de la Rue obtained by the action of nitric acid on car-

* Deut Chem. Ges. Ber., iv, 655—658.

minic acid. This they prepare by gradually adding finely powdered carmine to boiling nitric acid (sp. gr. 1·37) as long as the violent evolution of red vapours lasts. On cooling, the liquid solidifies to a mass of crystals of oxalic acid and nitrococcusic acid, which are separated by recrystallisation from very dilute nitric acid. The nitrococcusic acid is thus obtained in large silvery plates. On heating it with water in closed tubes to 180°, it splits up into carbon dioxide and *trinitrocresol*, $C_7H_4(NO_2)_3OH$, identical with that which Duclos obtained from coal-tar cresol. This reaction shows that nitrococcusic acid is one of the isomeric trinitrocresotic acids, and that the colouring matter of cochineal contains methylated benzene residues.

On heating a solution of carmine in concentrated sulphuric acid, the yellowish-red colour of the solution changed at 120° into violet, carbon dioxide and sulphur dioxide being evolved at the same time. After the temperature had been kept for some time at 140°—150°, the liquid was poured into cold water, when a brown precipitate was obtained, which was purified by washing, drying, exhausting with boiling alcohol, and evaporating the solution. This new colouring matter, which the authors call *ruficoccin*, is very sparingly soluble in cold water; it dissolves in alcohol with a fine yellow fluorescence; when heated it gives off red vapours, which condense to yellowish-red needles. Its composition is $C_{16}H_{12}O_6$, and as its formation and properties are very similar to those of rufigallic acid, it appears probable that this acid is a derivative of dimethyl-anthracene, having the following constitution:—

$$C_{14}H_2\left\{\begin{array}{l}(CH_3)_2\\(OH)_4\\(O_2)''.\end{array}\right.$$

On heating it with zinc-dust, a solid hydrocarbon is formed, which sublimes in white plates melting at 190°.

Ruficoccin has nearly the same composition as coccinin, which Hlasiwetz and Grabowsky obtained by fusing carmine-red with caustic potash, and the latter compound behaves like a hydroquinone of ruficoccin. It oxidises when exposed to the air, and shows after oxidation the same reactions as ruficoccin. Besides coccinin, Hlasiwetz and Grabowsky obtained succinic acid, which, as they believe, was derived from the glucose of carmine red; but from the last researches of Baeyer on phenol colours (p. 910) it appears not unlikely that carmine-red is a derivative of succinic acid, or an acid which yields succinic on fusion with caustic potash.

C. S.

On the Decomposition of Grape-sugar by Cupric oxide in Alkaline Solutions. By AD. CLAUS.*

THIS long paper is mainly devoted to a detailed criticism of the work of Reichardt and of Felsko on the same subject. The author shows that the chemists named took no adequate precautions to ascertain the purity or even approximate simplicity of the bodies they analysed under the names of gummic acid and various gummates, and quotes experiments of his own to show that the so-called gummic acid is merely impure tartronic acid. He states that the result of his own experiments is, that the products of the oxidation of grape-sugar by cupric oxide in alkaline solution are:—

1. Formic and acetic acids.

2. A mixture of non-volatile acids, containing tartronic acid, which can be obtained crystallised in the free state, and the salts of which are also crystallisable; then at least one acid, which, when boiled in aqueous or ammoniacal solution, easily decomposes, with formation of brown humus-like bodies; and, lastly, at least one acid which is uncrystallisable, and gives salts which dry up to a gummy mass.

3. A gum-like body.

The author then describes experiments on the influence of variations of the quantity of tartrate and of alkali, and of the concentration of the liquids, on the proportions between cupric oxide and the grape-sugar oxidised by it in Fehling's sugar-test. These experiments show that, in presence of a great excess of tartrate or of alkali, or in absence of the usual excess of the one or the other, or of both, exactly the same results are obtained. 5 molecules of cupric oxide are exactly reduced by 1 molecule of grape-sugar, $C_6H_{12}O_6$. Also, that 1 molecule of tartrate suffices to hold in solution 2 molecules of cupric oxide, whatever the excess of alkali. On long standing, however, the solution so made deposits a small quantity of an indistinctly crystalline salt, and, on boiling, deposits all its oxide of copper. When 1 molecule of tartrate to 1 mol. of cupric oxide is employed, the azure-blue solution can be boiled with excess of alkali without decomposition, and can be employed for the estimation of sugar.

The quantity of alkali neutralised by the acids proceeding from the oxidation of 1 molecule of grape-sugar was found to be about 1 molecule, but the variations in the numbers establishing this point were somewhat considerable.

C. H. G.

* J. pr. Chem. [2], iv, 63—96.

On a New Sweet Volatile Principle found in the Caoutchouc of Borneo. By AIMÉ GIRARD.*

THIS caoutchouc yields a new saccharine substance—designated by the author as *bornesite*—which is crystalline, very soluble in water, slightly soluble in alcohol, melts at 175° without alteration, and, like dambonite (p. 811), sublimes at 205° with slight decomposition. It does not ferment, neither does it reduce the potassio-tartrate of copper, but acquires the property of reducing this reagent by being boiled for several minutes with water slightly acidulated. Treated with a mixture of sulphuric and nitric acids, it forms a nitrated product, insoluble in water, soluble in alcohol, from which it is deposited in the crystallised state, fusible at 30°—35°, and detonating loudly when struck.

Bornesite has the composition $C_7H_7O_6$, and when heated to 120° in a closed vessel with fuming hydriodic acid, decomposes, like dambonite, into methyl iodide and dambose—

$$\underset{\text{Bornesite.}}{C_7H_7O_6} + HI = CH_3I + \underset{\text{Dambose.}}{2C_3H_6O_3}.$$

Dambonite and dambose have no effect upon polarised light, but bornesite possesses a rotatory power of 32° to the right, or nearly half that of pure cane-sugar under similar circumstances. Dambonite and bornesite may be considered as dambosates of methyl, the combination of two molecules of dambose in bornesite creating in the latter the power of rotating a ray of polarised light.

J. B.

Presence of Milk-sugar in a Vegetable Juice. By G. BOUCHARDAT.†

BY extracting sugar obtained from the juice of the sapodilla (*Achras Sapota*) with boiling alcohol, a crystalline substance is obtained, which, after being twice recrystallised from water, possesses all the properties of milk-sugar. It is hard, crunches between the teeth, is slightly sweet, melts at 204°, and gives off gas if this temperature be maintained for some time; it is soluble at the ordinary temperature to the extent of about 14 parts to 100 parts of water, and its solution rotates polarised light to the same degree as milk-sugar; heated with potash it turns brown; it reduces potassio-tartrate of copper, but does not undergo alcoholic fermentation by contact with beer-yeast under ordinary circumstances; it is precipitated by ammoniacal acetate of lead, and when treated with five times its volume of dilute nitric acid produces a certain quantity of mucic acid.

The mother-liquor from which the above substance is obtained

* Compt. rend., lxxiii, 426—429. † Compt. rend., lxxii, 462—464.

yields crystals possessing all the physical and chemical properties of cane-sugar.

The relative proportions of cane-sugar and milk-sugar in the substance employed are as 55 to 45.

The author also states that on treating the extract juice of ripe sapodilla fruit with acetate of lead, precipitating the saccharine matters with ammoniacal acetate of lead, and decomposing the precipitate with sulphuretted hydrogen, the filtered liquor concentrated to a syrup, purified by solution in alcohol, and subsequently treated with dilute nitric acid, readily yields crystals of mucic acid.

J. B.

On the Production of Ammonia in Alcoholic Fermentation. By M. DUBRUNFAUT. (Compt. rend. lxxiii, 459—462.)

The Products of the Electrolysis of Potassium Acetate. By TH. KEMPT and H. KOLBE.*

IT was shown by Prof. Kolbe twenty-two years ago that the main products of the electrolysis of a concentrated aqueous solution of potassium acetate are dimethyl and carbonic anhydride; at the same time it was noticed that a small quantity of a gas possessing an ethereal odour, and supposed to be methyl oxide, was formed. The authors have carefully re-examined this reaction. The electrolysis was effected by six powerful Bunsen elements, and the gas evolved at the positive pole first dried by calcium chloride, then passed through a tube surrounded by a freezing mixture, next through potash, and finally through concentrated sulphuric acid. A volatile liquid of varying boiling point condensed in the cooled tube, which proved to be a mixture of methyl acetate, formate, and carbonate. It was further found that ethylene was mixed with the dimethyl, from which it may have been formed by oxidation:—

$$CH_3.CH_3 + O = \left.\begin{matrix} CH_3 \\ H \end{matrix}\right\} C + OH_2.$$

A considerable quantity of the ethylene passed unabsorbed through the sulphuric acid and was converted into dibromide. The sulphuric acid gradually became darker as the gas bubbled through it, and eventually contained an organic sulpho-acid believed to be isethionic acid.

The dimethyl, purified as far as possible, was decomposed by a series of induction sparks; the volume of the gas became trebled, carbon being separated. The hydrogen formed burnt with a dis-

* J. pr. Chem. [2], iv, 46.

tinctly luminous flame, possibly due to the presence of traces of acetylene.

H. E. A.

Electrolysis of Phthalic Acid. By E. BOURGOIN.*

I. *Free Phthalic Acid.*—An aqueous solution of this acid is a bad conductor of the current. At the end of two days, with the aid of ten Bunsen elements, only 36·5 c.c. of gas were collected at the positive pole; this gas proved to be pure oxygen. On analysing the liquid in each compartment, at the termination of the experiment, it was found that a concentration of the solution had taken place at the positive pole, and that the quantity of acid electrolysed corresponded to the oxygen evolved. In one experiment:—

10 c.c. of the original liquid neutralised 15·5 c.c. of baryta solution after the electrolysis:—
10 c.c. of the liquid at the positive pole neutralised 21·5 c.c.;
10 c.c. „ „ negative „ „ 9·5 c.c.

Thus the water is not decomposed by the current; the acid alone is split up, according to the equation:—

$$C_8H_6O_4 = (C_8H_4O_3 + O) + H_2;$$

at the positive pole:—

$$(C_8H_4O_3 + O) + H_2O = C_8H_6O_4 + O.$$

II. *Neutral Potassium Phthalate.*—A concentrated solution of this salt is readily electrolysed. Hydrogen only is liberated at the negative pole, and the liquid in the corresponding compartment becomes strongly alkaline; at the positive pole, oxygen, together with appreciable quantities of carbonic anhydride and carbonic oxide, is evolved, and a crystalline layer of pure phthalic acid is deposited on the electrode. The composition of the gas, after 48 hours, was:—

$$CO_2—5·3;\ CO—5·5;\ O—89·2.$$

The carbonic oxide and anhydride are, no doubt, the result of the oxidation of a small quantity of acid at the moment of formation.

III. *Potassium Phthalate and Alkali.*—In the hope of obtaining phenylene, the author operated on a concentrated solution of potassium phthalate mixed with potassium hydrate. The mixture, $4C_8H_6O_4.KHO$, suffered exactly the same decomposition as the neutral salt, and the same negative result was obtained with a mixture of equivalent quantities of salt and alkali.

* J. Pharm. Chim. [4], xiii, 376–380.

Gallic and *pyrogallic* acids are oxidised with great readiness by electrolysis. At first no oxygen is evolved at the positive pole, it being entirely absorbed; afterwards carbonic anhydride is evolved in large quantity, and eventually a mixture of this gas with oxygen and carbonic anhydride.

H. E. A.

On Silicopropionic Acid. By C. FRIEDEL and A. LADENBURG.*

THE starting point for the preparation of this compound is the *monochlorhydrin of silicic ether*, $SiCl(OC_2H_5)_3$, which Friedel and Crafts obtained by heating silicic chloride with silicic ether. This chlorhydrin the authors prepare by a more simple process. They add 3 mol. of absolute alcohol, drop by drop, to 1 mol. of silicic chloride. After the reaction is over, the product is distilled and heated for some hours to 160°. By fractional distillation a large yield of the pure compound, which the authors propose to call *chloride of triethyl-silicic acid*, is obtained.

By adding sodium to a mixture of this compound with zinc-ethyl, and gently heating, a reaction is set up, gases being evolved, which in the beginning of the operation contain chlorides; afterwards only hydrocarbons are given off.

On distilling the product, metallic zinc separates out; the distillate consists chiefly of *ethyl orthosilico-propionate*, $SiC_2H_5(OC_2H_5)_3$, which is obtained pure by fractional distillation. It is a colourless liquid, smelling like camphor, and boiling at 158·5°. It is insoluble in water, but mixes with alcohol and ether. The mode of formation is expressed by the equation—

$$2SiCl(OC_2H_5)_3 + Zn(C_2H_5)_2 = ZnCl_2 + 2SiC_2H_5(OC_2H_5)_3;$$

but besides this reaction, other secondary ones take place at the same time, by which the yield of the new compound is decreased to about 33 per cent. of the chloride employed.

In some operations, a liquid having the same boiling point, but containing more carbon and hydrogen, was obtained. When one mol. of zinc-ethyl and one of the chloride were employed, the liquid boiling at 155°—156° had nearly the composition $Si(C_2H_5)_2(OC_2H_5)_2$. From this it appears that the zinc-ethyl acts at the same time as a reducing agent, and this is further proved by the fact that on heating the trichlorhydrin, $SiCl_3(OC_2H_5)$, with zinc-ethyl, silicon-ethyl is formed.

On heating silicopropionic ether with a concentrated aqueous solution of caustic potash, a violent reaction sets in, which is over in a few minutes. On neutralising the liquid, which consists of two layers, both

* Ann. Chem. Pharm., clix, 259—274.

soluble in water, with hydrochloric acid, and adding ammonia, a white flocculent precipitate is formed, which consists of *silicopropionic acid*, $C_2H_5.SiO_2H$, mixed with silica.

When ortho-silico-propionic ether is heated with phosphorus trichloride, volatile chlorides are formed, which are decomposed by water, the product of the reaction being a mixture of phosphoric acid, amorphous phosphorus, silica, and silicopropionic acid.

The only way of obtaining the latter compound free from silica is to heat the ether with acetyl chloride to 180°, when the following reaction takes place:—

$$3C_2H_3OCl + SiC_2H_5(OC_2H_5)_3 = SiC_2H_5Cl_3 + 3(C_2H_3O.OC_2H_5).$$

By acting with water on the trichloride thus formed, the pure acid is obtained. It is a white powder resembling silica, from which, however, it is easily distinguished by being combustible, and leaving a grey ash, which does not become quite white, even when heated in oxygen. Silicopropionic acid is insoluble in water, but soluble in warm concentrated potash solution. On adding hydrochloric acid to this solution, none, or only a part of the acid is precipitated; but on evaporating to dryness, it is left as an insoluble residue. Silicopropionic acid also differs from silica by being insoluble in boiling caustic soda. From its alkaline solutions it is only partially precipitated by carbonic acid.

Many metallic salts form precipitates when added to a weak alkaline solution of the acid; but they always contain oxides.

By employing Graham's method of dialysis, a pure aqueous solution of the acid was obtained, in which barium and lead acetate produced precipitates, containing after washing, only such small quantities of the metal, that it was impossible to assign formulas to them. Silicic acid behaves exactly in the same way.

Silicopropionic acid is the first representative of a new class of organo-silicic acids, containing the group SiO_2H in the place of carboxyl CO_2H.

C. S.

Conversion of Acetone into Lactic Acid. By E. LINNEMANN and V. VON. ZOTTA.*

WHEN dichloracetone is heated with an excess of water to 200° for six hours, it is completely decomposed. On evaporating the liquid on a water-bath, a brown syrup is left behind, which contains a large quantity of lactic acid. The dichloracetone employed boiled at 115°—117°, but contained only 47·7 per cent. of Cl, instead of 53·9 per cent.

C. S.

* Ann. Chem. Pharm., clix, 247—251.

Oxidation of α-Naphthyl-carboxylic Acid. By CARSTANJEN and SCHERTEL.*

ACCORDING to the theory of Erlenmeyer and Gräbe on the constitution of naphthalene, the carboxyl-acid of this hydrocarbon should yield by oxidation a benzol-tricarboxyl acid, or perhaps, like naphthalene itself phthalic acid.

By the action of potassium permanganate in presence of very little water, a strong reaction is set up in a few minutes, and the alkaline filtrate treated with hydrochloric acid, gives only a little acid, difficultly soluble in water. This may be unaltered naphthyl-carboxylic acid, but it appears to melt constantly at 156°, whereas the original acid melted at the normal temperature, 139°—140°. The solution in hydrochloric acid evaporated to dryness, and exhausted with ether gives a non-crystallisable sour syrup, which precipitates lead acetate; the lead salt decomposed by hydric sulphide gives an acid readily soluble in water, crystallising in fine needles, and yielding a soluble potassium salt, and an insoluble barium salt.

The action of nitric acid seems to produce a nitro-acid, which is under investigation.

C. R. A. W.

On the Constitution of Chrysanisic Acid. By H. SALKOWSKY.†

THE dinitro-oxybenzoic acid formed by the action of nitrous acid upon chrysanisic acid‡ is bibasic. The following salts and ethers have been analysed:—

$C_6H_2(NO_2)_2OHCO_2K$ $\quad$ $C_6H_2(NO_2)_2OKCO_2K + 2H_2O$.
$[C_6H_2(NO_2)_2OHCO_2]_2Ba + 5H_2O$ $\quad$ $[C_6H_2(NO_2)_2OCO_2]_2Ba_2 + 7H_2O$.

A monobasic silver-salt could not be obtained.

The *mono-ethyl ether* $C_6H_2(NO_2)_2OHCO_2(C_2H_5)$, when perfectly pure, melts at 87°, and is not coloured yellow by exposure to light. On mixing its alcoholic solution with an alcoholic solution of potash, the salt $C_6H_2(NO_2)_2OKCO_2(C_2H_5)$ is formed, which, as well as the corresponding silver-salt obtained from it by double decomposition, can be recrystallised from hot water, without suffering decomposition. On treating the silver-salt with ethyl iodide, the *diethyl ether* is formed, which crystallises in colourless, shining, narrow leaflets, melting at 59°. Both ethers are decomposed by treating them with an aqueous solution of potash, or heating them with an alcoholic potash-solution, the original acid being formed again; but with a cold alcoholic potash-solu-

* J. pr. Chem. [2], iv, 49. † Deut. Chem. Ges. Ber., iv, 652—655.
‡ Page 556 of this volume.

tion, the diethyl ether yields a magenta-red liquid, which on standing becomes colourless, with formation of potassium dinitro-oxybenzoate. By passing hydrochloric acid into it, the diethyl ether is reproduced; the red solution contains therefore potassium ethyl dinitro-oxybenzoate, a compound which cannot be obtained in the solid state.

By acting with ammonia on the diethyl ether, chrysanisic acid is formed again, and on the other hand, when chrysanisic acid or its ether is boiled with an alkali, ammonia is evolved, and dinitro-oxybenzoic acid is obtained.

These reactions prove conclusively that chrysanisic acid contains the amido-group, the basic character of which is completely hidden by the presence of one carboxyl group and two nitro-groups. But how this amido-group has been formed, and how it can exist under the conditions under which chrysanisic acid is obtained, has to be explained by further researches. It is possible that the large quantity of nitroanisic acid which is not acted upon during the reaction, exerts a protecting influence, as pure chrysanisic acid is easily converted into picric acid by heating it with fuming nitric acid.

C. S.

Researches upon the Crenic and Apocrenic Acids contained in the Mineral Waters of Forges-les-Eaux, Seine-Inférieure. By C. Boutigny.*

The author believes that the medicinal waters of Forges-les-Eaux contain ferrous salts of crenic and apocrenic acids. On exposure to air the waters deposit an insoluble ferric compound, from which crenic acid can be extracted by boiling with caustic potash, and precipitating the solution with hydrochloric acid. The purified crenic acid is capable of dissolving ferrous carbonate. The source of the waters is a peaty stratum, underlain by a vein of iron pyrites.

R. W.

On Chloro- and Cyano-acetone. By L. Glutz and E. Fischer.†

Chlorine produces with perfectly dry acetone principally monochloracetone $CH_2Cl-CO-CH_3$, boiling at 119°—120°; this compound is identical with that obtained electrolytically: with potassium iodide it yields iodacetone as an oily non-distillable fluid, becoming gelatinous on long standing.

Dichloracetone obtained by Fittig's process by passing chlorine into acetone heated at last on the water-bath until saturated, boils at the same temperature as monochloracetone, viz., 119°—120°, and contains none of this latter substance, contrary to Kriwaksin's statement.

* Compt. rend., lxxiii, 247—249. † J. pr. Chem. [2], iv, 52.

This dichloracetone yields with potassium cyanide in aqueous solution, a solid substance crystallisable from water: monochloracetone thus treated gives an oily brown fluid, solidifying after standing for some days, and consisting of monocyanacetone. The compound thus obtained from dicyanacetone has been examined by Mulder,* who ascribed to it the formula, $C_9H_{12}Cl_6O_3NH_4HCN$: the authors conclude from their analyses that the formula is $C_7H_9Cl_4O_2N$.

The dichloracetone thus produced is unsymmetrical in structure, being $CHCl_2-CO-CH_3$; no definite bodies could be isolated from the bye-products of the action of chlorine on acetone, so that apparently the symmetrical dichloracetone $CH_2Cl-CO-CH_2Cl$, which has a much higher boiling point, is not formed in this way. This symmetrical dichloracetone is obtainable by the oxidation of dichlorhydrin, $CH_2Cl-CH(OH)-CH_2Cl$ with potassium dichromate and sulphuric acid, the yield being about 50—60 per cent. of the theoretical quantity; it boils at 170°—171°, and gives a well crystallising compound with sodium-hydrogen sulphite: with potassium iodide and potassium sulphocyanate it gives crystallisable compounds, but with aqueous potassium cyanide only a brown tarry fluid speedily becoming black: with solid powdered potassium cyanide, however, an ethereal solution of the dichloracetone produces a body crystallisable from alcohol, and isomeric with that produced by the action of the unsymmetrical dichloracetone; to these bodies the authors ascribe the following formulæ—

From the symmetrical dichloracetone.

$$\left.\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix}\right\}C\left.\begin{matrix}OH\\O\\CN\end{matrix}\right\}\left.\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix}\right\}C$$

Tetrachloro-diacetone-cyanhydrin.

From the unsymmetrical dichloracetone.

$$\left.\begin{matrix}CH_3\\CHCl_2\end{matrix}\right\}C\left.\begin{matrix}OH\\O\\CN\end{matrix}\right\}\left.\begin{matrix}CHCl_2\\CH_3\end{matrix}\right\}C$$

Isotetrachloro-diacetone-cyanhydrin.

each being formed by the reaction—

$$2C_3H_4Cl_2O + KCN + H_2O = KOH + C_7H_9Cl_4O_2N,$$

the diacetone-cyanhydrin of Urech being the connecting link between the two, viz.:—

$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}C\left.\begin{matrix}OH\\O\\CN\end{matrix}\right\}\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}C$$

As this last body splits by the action of acids into acetone, ammonia, and oxyisobutyric acid, the authors hope to obtain an analogous reaction with the two tetrachloro-diacetone-cyanhydrins just described; from the symmetrical dichloracetone derivative, the body $(CH_2Cl)\equiv C(OH)-$

* Zeit. f. Chem. [2], iv, 51.

CO(OH) should result; by acting on this with cyanide, &c., so as to replace the chlorine groups by carboxyl, they hope to obtain citric acid—

$$\begin{array}{l} CH_2.CO(OH) \\ C(OH).CO.(OH) \\ CH_2.CO(OH). \end{array}$$

C. R. A. W.

On Monochlorinated Ethyl Chloride. By W. WALTERS.*

A LARGE quantity of ethylidene chloride was prepared by the action of chlorine on ethyl chloride; by rectification alone this body could not be obtained pure; but by treatment with mercury a pure body boiling constantly at 64° was obtained, the mercury destroying ethyl chloride even at common temperatures, with evolution of diethyl.

Reactions analogous to that of M. Kind, whereby only one chlorine atom is replaced (as by the action of alkaline sulphites, whereby chlorethyl sulphuric acid is formed), have not yet been observed. Silver oxide causes the reduction of silver and formation of acetate; so also potash ley after some days' action forms acetate, aldehyde being without doubt the first product of the action, and converted into acetic acid by atmospheric oxidation. Alkaline sulphydrates and monosulphides similarly produce sulphaldehyde.

By heating with acetates, preferably with the lead salt, at a temperature of 150°—160°, an ether is obtained which is crystallisable, but has not yet been procured pure enough for analysis: if only one atom of chlorine is replaced, a chlorinated ethyl alcohol isomeric with ethylene oxychloride should be obtainable from this compound.

C. R. A. W.

On Bromobenzonitrile. By C. ENGLER.†

THIS compound is formed only in small quantities by the direct action of bromine on benzonitrile; but it is easily obtained from bromobenzoic acid, which by passing hydrochloric acid gas through its alcoholic solution, is first converted into ethyl bromobenzoate, a strongly refracting liquid boiling at 259°. On treating it with an alcoholic solution of ammonia, it is not completely converted into bromobenzamide, even when heated for some days to 150°. By using aqueous ammonia a portion of the amide formed is converted into ammonium bromobenzoate before all the ether is acted upon. To prepare the amide it is best to heat one volume of the ether with one vol. of alcoholic and two vols. of aqueous ammonia for 24 hours to 130°—140°.

* J. pr. Chem. [2], iv, 57. † Deut. Chem. Ges. Ber., iv, 701—707.

Bromobenzamide crystallises from dilute alcohol in colourless pearly scales, melting at 150° and subliming at a higher temperature. On distilling it with phosphorus pentoxide, bromobenzonitrile is formed, a crystalline solid, melting at 38° and boiling at about 225°. From ether it crystallises in lance-shaped needles.

By replacing the bromine in this compound with methyl, a nitrile would be formed, from which one of the toluic or phthalic acids could be obtained, and thus the position of the bromine in bromobenzoic acid would be ascertained. But bromobenzonitrile is not acted upon by methyl iodide and sodium in presence of ether, nor did the author succeed in substituting the bromine by cyanogen. As v. Meyer has since obtained isophthalic acid from bromobenzoic acid, the author has not pursued this research.

C. S.

On Glucoso-phosphoric Acid. By D. Amato.*

The author has examined a strongly acid residue, which Schiff obtained in the course of his researches on the constitution of salicin and helicin, by treating the latter substance with phosphorus oxychloride, digesting the resulting mass with alcohol, and evaporating. This residue—which must have been produced by the mutual action of hydrochloric acid, phosphoric acid, and glucose, resulting from the decomposition of helicin in presence of phosphorus oxychloride—was rendered slightly alkaline with sodium carbonate, then evaporated to a syrup, and digested with alcohol, which partly dissolved it, leaving a residue of chloride and phosphate of sodium. On distilling off the alcohol, evaporating the residue at a very gentle heat, and treating it with absolute alcohol, there remained a quantity of sodium phosphate nearly free from chloride. On again distilling off the alcohol and evaporating, a residue was obtained which dissolved completely in absolute alcohol; and this substance, when freed from alcohol and evaporated under the air-pump, formed a very hygroscopic mass, which became pasty on exposure to moist air, but was extremely friable and easily pulverised when dry.

This substance is very soluble in water and alcohol, but insoluble in ether; it has a yellowish tinge when first obtained, but may be rendered perfectly white by boiling with animal charcoal. It does not precipitate barium chloride or lead acetate, and may be purified from a small quantity of phosphoric acid adhering to it in the form of sodium phosphate, by treating it with lead acetate, evaporating, dissolving the residue in absolute alcohol, evaporating off the alcohol, and precipitating the excess of lead with hydrogen sulphide.

* Gazzetta chemica Italiana, i, 56—60.

The aqueous solution does not give the reaction of phosphoric acid with magnesium salts, ammonia and sal-ammoniac; neither does it exhibit the reaction of glucose with a cupro-potassic solution. But if it be previously boiled with a sufficient quantity of sulphuric acid, taking care not to carry the action so far as to destroy the glucose, the solution will then exhibit very plainly the reactions of phosphoric acid and of glucose. The presence of phosphoric acid may also be demonstrated by incinerating the substance, oxidising the residue with nitric acid, and testing as above with a magnesium salt and ammonia.

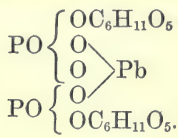
Quantitative determinations of the ash (sodium pyrophosphate) thus obtained and of the phosphoric acid contained in it, have shown that the substance in question has the composition of disodic glucoso-phosphate.

$$C_6H_{11}O_5Na_2PO_4 = \left\{ \begin{array}{l} CHO \\ | \\ (CH.OH)_4 \\ | \\ CH_2.O.PO\begin{array}{l}\diagup ONa \\ \diagdown ONa\end{array} \end{array} \right.$$

A lead salt was prepared by treating the sodium salt with excess of dilute sulphuric acid, digesting with alcohol to separate the acid sodium salt thereby produced, evaporating off the alcohol, neutralising with sodium carbonate, and finally with precipitated oxide of lead, and evaporating the filtered solution. A crystalline salt was thus obtained having an alkaline reaction, and yielding by incineration 75·4 per cent. ash, agreeing with the formula—

$$C_6H_{11}O_5Pb_2PO_5 = \left\{ \begin{array}{l} CHO \\ CHOH \\ CHOH \\ \left.\begin{array}{l}CHO \\ CHO\end{array}\right\rangle Pb \\ CH_2O.PO\left\langle\begin{array}{l}O \\ O\end{array}\right\rangle Pb + H_2O. \end{array} \right.$$

By treating sodium glucoso-phosphate with sulphuric acid, &c., in the same manner as above, excepting that the last traces of acidity were not neutralised with oxide of lead, a slightly acid crystalline lead-salt was obtained, insoluble in ether, very soluble in water and in alcohol, and crystallising from the latter in magnificent setaceous needles, melting at 187°. This purified salt yielded 51·5 per cent. ash, agreeing with the formula $C_{12}H_{22}O_{10}PbP_2O_7$. It may be supposed to be formed from two molecules of glucoso-phosphoric acid, which, under the influence of the lead salt, unite together, with elimination of 1 mol. water. Such a constitution is represented by the formula—



In accordance with this, it is found that the ash gives the reactions of plumbic metaphosphate, whereas that of the former salt gives those of the pyrophosphate.

The last described salt heated to 150° in sealed tubes with ethyl iodide, was converted into lead phosphate and another substance, probably identical with that which Berthelot* obtained by heating cane-sugar in sealed tubes with potash and ethyl bromide.

H. W.

Action of Cyanogen Chloride, gaseous and solid, on Benzylic Alcohol. By S. Cannizzaro.†

Gaseous cyanogen chloride liquefied by cooling, was mixed in tubes drawn out in the middle, for convenience of sealing, and immersed in a freezing mixture with benzylic alcohol, in the proportion of CNCl to $2C_7H_8O$; and the tubes, after being sealed, were exposed for an hour or two to the temperature of the air. The contents became hot and acquired a yellowish colour, and, on subsequent cooling, solidified to a crystalline mass, mixed in the lower parts with a small quantity of white amorphous substance. The tubes were then opened (after again immersing them in the freezing mixture to prevent loss from projection) and the contents, liquefied by gentle warming, were poured into a flask and distilled under a pressure of about 10 mm., first in the water-bath and finally in a bath of salt water. Benzylic chloride then passed over, and the residue solidified to a crystalline mass containing benzylic carbamate, which was purified by repeated crystallisation from ether till it dissolved completely therein, and finally by crystallisation from boiling water. The matter insoluble in ether (the white amorphous substance above mentioned), consisted of sal-ammoniac, and an organic substance insoluble in water, alcohol, and ether, slightly soluble in carbon bisulphide, the quantity of which was too small for satisfactory examination.

If an excess of cyanogen chloride be added, the reaction takes place in the same way, the excess partly remaining unaltered, and being partly converted into solid cyanogen chloride; a small quantity of hydrochloric acid is also frequently evolved.

The principal and final action of gaseous cyanogen chloride on

* Ann. Chim. Phys., [3], lx, 93; Jahresb. f. Chem., 1860, p. 509.

† Gazzetta chimica Italiana, i, 33—38.

benzylic alcohol may therefore be represented by the following equation :—

$$\underset{\text{Benzylic alcohol.}}{2C_7H_8O} + \underset{\text{Cyanogen chloride.}}{CNCl} = \underset{\text{Benzylic carbamate.}}{CO\left\{\begin{matrix} NH_2 \\ OC_7H_7 \end{matrix}\right.} + \underset{\text{Benzylic chloride.}}{C_7H_7Cl.}$$

The same products are obtained with solid cyanogen chloride. When this substance is triturated in a mortar with benzylic alcohol, added drop by drop till the proportion amounts to $C_3N_3Cl_3$ to $6C_7H_8O$, the reaction commences with evolution of heat, a small quantity of hydrochloric acid being given off before the whole of the benzylic alcohol has been added; and on placing the mortar, after the reaction is terminated, in a steam-bath, decanting the liquid portion of the contents into a flask, and distilling as above, benzylic chloride passes over and benzylic carbamate remains behind. The solid residue in the mortar yields to ether another portion of the carbamate, and the portion insoluble in ether contains sal-ammoniac, together with a white substance slightly soluble in boiling water, crystallising therefrom in gelatinous flocks, and very similar in appearance to the substance which Habich obtained in preparing cyanuric acid by heating urea.

Benzylic carbamate, whether prepared with gaseous or with solid cyanogen chloride, crystallises in beautiful transparent colourless laminæ, melting at 86°, moderately soluble in warm water, from which it crystallises on cooling, more soluble in ether, extremely soluble in alcohol. When it is heated in a retort to 200°—230°, a very small portion sublimes unaltered, but the greater part is resolved into benzylic alcohol and cyanuric acid:

$$3CO\left\{\begin{matrix} NH_2 \\ OC_7H_7 \end{matrix}\right. = 3C_7H_8O + C_3N_3O_3H_3.$$

Solid cyanogen chloride heated with benzylic alcohol to higher temperatures (180°—200°) yields, in addition to benzylic chloride and sal-ammoniac, two new crystalline substances and scarcely a trace of benzylic carbamate. By repeated crystallisation from alcohol and ether, these two bodies are obtained, the one in slender, flexible, dazzling-white needles, melting at about 153°, and having nearly the composition of benzylic cyanate or cyanurate; the other in hard yellowish prisms, melting at about 143°, and containing about 75—76 p. c. carbon, 6·1 hydrogen, and 11·2 nitrogen, a composition agreeing approximately with the formula $C_{15}H_{14}N_2O$. This latter substance, treated with potash, yields a liquid base resembling dibenzylamine in odour and appearance. The author proposes to make a further examination of these two substances, with the view of ascertaining their relation to benzylic carbamate, from which they appear to be derived.

H. W.

On Monobenzyl-urea. By S. CANNIZZARO.*

IN his memoir on the *alkaloids derived from benzylic alcohol* (1865)†, the author stated that when benzylic chloride and potassium cyanate are heated together for a considerable time in an apparatus with reversed condenser, the alcohol then distilled off, and the residue treated with boiling water, an oily substance separates, which on cooling solidifies to a crystalline mass containing dibenzylurea. The aqueous solution contains the potassium chloride formed in the reaction, the carbonate resulting from decomposition of the cyanate, and monobenzylurea, $CO\left\{\begin{matrix}NH_2\\NHC_7H_7\end{matrix}\right.$; and on evaporating the solution to dryness over the water-bath, treating the residue with a large quantity of ether, and distilling off the ether, the monobenzylurea remains behind, and may be purified by recrystallisation either from water or from alcohol.

Monobenzylurea crystallises in long white needles, moderately soluble in water and in alcohol, more at high than at low temperatures; freely soluble in ether; it melts at 147°—147·5°, but begins at the same time to give off ammonia: hence after being once fused it melts at a lower temperature. When heated to about 200°, it slowly evolves ammonia and yields a white sublimate, which crystallises from alcohol in white needles, having the appearance, composition, and melting point (166°—167°) of dibenzylurea.

Both dibenzylurea and monobenzylurea may also be obtained with tolerable facility by heating urea, benzylic chloride, and alcohol together in an apparatus with reversed condenser, then distilling off the alcohol, and heating the residue with water. The dibenzylurea is contained in the oily insoluble portion of the product, while the monobenzylurea dissolves in the water, and may be separated and purified as above.

H. W.

Action of Urea Nitrate on Benzylic Alcohol. By G. CAMPISI and D. AMATO.‡

THE products of this reaction vary according to the temperature. When the two substances are heated together in a water-bath, or to any temperature below 120°, the chief products are dibenzylurea, $CH_2(C_7H_7)_2N_2O$—identical with that which Cannizzaro obtained by the action of potassium cyanate on benzylic chloride—and benzoic aldehyde; but when the temperature of the mixture is raised to

* Gazzetta chimica Italiana, i, 41.

† Giornale di Scienze naturali ed economiche. Vol. i. Palermo, 1865.

‡ Gazzetta chimica Italiana, i, 39.

130°—140°, the chief product is benzylic carbamate, together with a small quantity of another substance insoluble in cold ether, soluble in very strong alcohol and in boiling ether, from which it separates in crystals melting at 151°—152·5°. The authors do not, however, recommend this process for the preparation either of dibenzylurea or of benzylic carbamate, as the product in either case is but small in proportion to the quantity of benzyl alcohol consumed.

H. W.

On the Periodides of the Alkaloïds. (Continuation.)

By S. M. Jörgensen.*

The author has prepared and examined the following compounds :—

Piperine triiodide	$C_{34}H_{38}N_2O_6HI_3$.
Atropine triiodide.....	$C_{17}H_{23}NO_3HI_3$.
,, pentaiodide	$C_{17}H_{23}NO_3HI_5$.
Berberine triiodide	$C_{20}H_{17}NO_4HI_3$.
Theobromine tetraiodide	$C_7H_8N_4O_2HI_4$.

They were prepared by adding iodine dissolved in potassium iodide to a solution of the alkaloïd in aqueous or alcoholic hydrochloric acid ; or by dissolving the alkaloïd in excess of hydrochloric acid, adding potassium iodide, and leaving the mixture to slow oxidation and evaporation.

These periodides seem to resemble, in their general properties, the periodides of the strychnine and cinchona alkaloïds, already partially described in this Journal.†

Tetrethylphosphonium Triiodide.—This body is formed by adding to a warm alcoholic solution of tetrethylphosphonium iodide, 2 atoms of iodine in alcoholic solution, carefully avoiding excess of iodine. On slow cooling, crystals of triiodide separate out ; they appear in leaves, whose composition is expressed by $P(C_2H_5)_4,I_3$, of a brown colour and diamond-like brilliance, frequently of very large dimensions. The alcoholic solution of the crystals is decolorised by reducing agents.

Tetrethylarsonium Triiodide, $As(C_2H_5)_4I_3$.—When powdered arsenic is heated in sealed tubes with ethyl iodide to 200°, for about four hours, the tube becomes filled with large brown leafy crystals of the compound $As(C_2H_5)_4I,AsI_3$. By boiling these crystals with alcohol of 90 per cent., a dark brown liquid is obtained, yielding by spontaneous evaporation long brown laminæ, resembling in appearance the tetrethylphosphonium triiodide. They have the composition $As(C_2H_5)_4I_3$; their

* J. pr. Chem. [2], iii, 328—348. † See page 398.

alcoholic solution is decolorised by reducing agents, mercury for example.

A *triiodide of tetrethylstibonium* appears to exist, but its composition has not been determined.

Periodide of Triethylsulphine.—An attempt to form a definite periodide did not succeed. Iodine dissolved in potassium iodide, when added to an aqueous solution of iodide of triethylsulphine, produces a brown precipitate, which soon becomes a black tar. From potassium iodide, 2 atoms iodine, and 1 atom $S(C_2H_5)_3I$, a product is obtained which contains more iodine than a triiodide, less than a tetraiodide.

A postscript to the paper contains a description of a series of well crystallised double salts containing bismuth. The general formula of these compounds is $3R(C_2H_5)_4R'.2BiR'_3$ in which R = N, P, As or Sb; R′ = I, Br, Cl. The iodine compounds are red, or brownish red, the bromine compounds yellow, or occasionally brownish yellow, the chlorine compounds colourless.

The iodine derivatives are produced by precipitating a hot alcoholic solution of the periodide with potassio-iodide of bismuth, or with hydroiodide of bismuth. Thus the tetrethylammonium bismuth iodide $3N(C_2H_5)_4I.2BiI_3$.

$$3N(C_2H_5)_4I.I_2 + 3KI.2BiI_3 = 3KI.I_2 + 3N(C_2H_5)_4I.2BiI_3.$$

The ethylphosphonium, ethylstibonium, and ethylarsonium compounds were also made; they have a composition similar to that of the nitrogen salt:

$$3P(C_2H_5)_4I.2BiI_3.$$
$$3Sb(C_2H_5)_4I.2BiI_3.$$
$$3As(C_2H_5)_4I.2BiI_3.$$

The bromine and chlorine derivatives were prepared by precipitating the hot alcoholic solution of the periodide with a solution of bismuth hydrate in strong hydrobromic or hydrochloric acid respectively. The tetrethylammonium-bismuth-bromide is thus constituted:—$3N(C_2H_5)_4Br.2BiBr_3$; the chloride, $3N(C_2H_5)_4Cl.2BiCl_3$. Corresponding phosphorus, arsenic, and antimony compounds were also prepared and analysed. W. H. D.

Preparation of the Ethylene Bases on the large scale. By A. W. Hofmann.*

The bye-products in the manufacture of chloral contain, besides ethyl chloride, as Kraemer has found, large quantities of ethylene- and ethylidene dichloride. Now as the latter compound is not attacked by ammonia under 160°, the mixture of the higher-boiling chlorides furnishes an excellent material for the preparation of the ethylene

* Deut. Chem. Ges. Ber., iv, 666—668.

bases. On heating the fraction boiling between 70°—100° for eight or ten hours to 110° with an excess of alcoholic ammonia, the ethylene chloride is decomposed. After filtering to remove sal-ammoniac, the liquid is distilled. The residue crystallised from water yields a large crop of ethylenediamine chlorhydride, which crystallises in large shining needles. The mother-liquors, on distillation with caustic soda, first yield ethylenediamine, and the latter fractions contain the higher diamines and triamines.

C. S.

Action of Chloral on Aniline. By O. WALLACH.*

CHLORAL acts with great violence on aniline; on cooling, the product solidifies to a white crystalline mass, which by crystallisation from alcohol yields large fine crystals. This compound has basic properties; it is soluble in acids, and insoluble in alkalis, which on boiling decompose it. A similar compound is obtained from toluidine.

Whilst aldehyde and aniline hydrochloride act on each other with such violence that the mixture has to be cooled, chloral gives no reaction with the aniline-salt in the cold, and the action goes on but slowly even on heating. The product consists of the hydrochloride of a white base, which forms yellow salts with acids. The basic compound is readily decomposed by alkalis in the cold, an oily liquid having the smell of phenylic cyanide being formed.

C. S.

Action of Hydracids on the Quinine Alkaloïds. By W. ZORN.†

WHEN cinchonine sulphate was heated in sealed tubes with concentrated hydrochloric acid for some hours to 140°—150°, the contents of the tubes yielded on evaporation, crystals not unlike those of cinchonine sulphate, but differing therefrom essentially in their insolubility in acids. After one recrystallisation these crystals do not contain a trace of sulphuric acid; their solution is strongly acid, but is no longer fluorescent. They are anhydrous. Chlorine determinations prove that they contain three atoms of chlorine, two of which are readily and completely removed by silver nitrate, the third with difficulty. The mother-liquor from the above crystals yields on further evaporation a second crop of different aspect, but also free from sulphuric acid.

Quinine sulphate similarly treated gives crystals, which also do not contain any sulphuric acid; these yield a strongly acid solution, which is non-fluorescent, and coloured only very slightly green on addition of

* Deut. Chem. Ges. Ber., iv, 668, 669. † J. pr. Chem. [2], iv, 44.

chlorine water and ammonia. Potassium ferrocyanide produces a yellow precipitate, insoluble in excess, but soluble on boiling. The base is precipitated by ammonia, and is readily soluble in ether, also in an excess of ammonia and in boiling water. In its behaviour with ammonia and chlorine-water, and with ferrocyanide, this new body resembles cinchonine; like quinine, it is readily soluble in ether, but differs from both by its solubility in ammonia and in boiling water.

By the action of hydriodic acid on cinchonine sulphate, products are obtained, the examination of which, and of the above, the author is prosecuting.

H. E. A.

Contributions to the History of the Opium Alkaloïds. Part II. By C. R. A. WRIGHT.*

THIS paper treats of the products formed from codeine and its derivatives by the long-continued action of hydrobromic acid, methyl bromide being evolved in every case. By the action of hydrobromic acid on bromo-tetracodeine hydrobromide, four molecules of methyl bromide are eliminated, and a homologous base, bromotetramorphine, is produced, by the reaction—

$$\underset{\text{Bromotetracodeine.}}{C_{72}H_{83}BrN_4O_{12}} + 4HBr = 4CH_3Br + \underset{\text{Bromotetramorphine.}}{C_{68}H_{75}BrN_4O_{12}}.$$

By the action of hydrochloric acid in the cold on bromotetramorphine, the corresponding chlorinated base, chlorotetramorphine, is formed; and by interrupting the action of hydrobromic acid on codeine at a certain point, a base intermediate between bromotetramorphine and bromotetracodeine appears to be formed; and this, by the action of hydrochloric acid, is converted into the corresponding chlorinated base, chlorodicodeine-dimorphine. The results obtained indicate the probable existence of the following ten bases, five of which (viz., those named) have been obtained and analysed, as well as their platinum salts, &c.

Bromotetracodeine.....	$C_{72}H_{83}BrN_4O_{12}$.
	$C_{71}H_{81}BrN_4O_{12}$.
	$C_{70}H_{79}BrN_4O_{12}$.
	$C_{69}H_{77}BrN_4O_{12}$.
Bromotetramorphine	$C_{68}H_{75}BrN_4O_{12}$.
Chlorotetracodeine.....	$C_{72}H_{83}ClN_4C_{12}$.
	$C_{71}H_{81}ClN_4O_{12}$.
Chlorodicodeine-dimorphine	$C_{70}H_{79}ClN_4O_{12}$.
	$C_{69}H_{77}ClN_4O_{12}$.
Chlorotetramorphine	$C_{68}H_{75}ClN_4O_{12}$.

* Proc. Roy. Soc., xix, 504.

It was not thought worth while to attempt the formation of the missing members of the series, owing to the extreme similarity in properties between those already obtained, and the uncertainty as to purity arising from their physical characters and high formulæ.

By the action of hydrobromic acid on bromocodide, methyl bromide is formed, and simultaneously bromotetramorphine, and apparently a base, dioxymorphine, homologous with deoxycodeine; this latter, like its homologue, much resembles apomorphine in chemical characters, but produces no vomiting; it is doubtful whether deoxymorphine has been obtained perfectly free from deoxycodeine. Its formula is $C_{17}H_{19}NO_2$. From these results, taken in conjunction with former ones, the author ascribes the following formulæ to the corresponding bases:—

Codeine.

$$C_{17}H_{17}NO \left\{ \begin{array}{l} O.H \\ O.CH_3. \end{array} \right.$$

Bromocodide.

$$C_{17}H_{17}NO \left\{ \begin{array}{l} Br \\ O.CH_3. \end{array} \right.$$

Deoxycodeine.

$$C_{17}H_{17}NO \left\{ \begin{array}{l} H \\ O.CH_3. \end{array} \right.$$

Deoxymorphine.

$$C_{17}H_{17}NO \left\{ \begin{array}{l} H \\ O.H. \end{array} \right.$$

By the action of hydrobromic acid on deoxycodeine, deoxymorphine does not seem to result, the only product being a black substance unfit for analysis, together with a little methyl bromide.

Dr. Michael Foster has examined the physiological action of the foregoing derivatives, and finds that the chloro- and bromotetracodeine and tetramorphine salts produce in adult cats a condition of great excitement, almost amounting to delirium in younger animals; a want of co-ordination of muscular movements follows, terminating in sleepiness, stupor, and death. Paralysis of the inhibitory fibres of the pneumogastric appears to be produced in cats and dogs; with *rabbits* all these salts appear to be almost inert.

Deoxycodeine and deoxymorphine salts are absolutely destitute of emetic properties; in adult cats they produce convulsions of an epileptic character, followed by the symptoms observed in the case of the tetra-bases. No marked difference could be detected between the hydrobromides and hydrochlorides of either base; whereas with the tetra-bases, the morphine-compounds appeared to be rather more potent than their higher homologues.

C. R. A. W.

Researches on the Constitution of Piperine and its Decomposition Products, Piperic Acid and Piperidine. By RUD. FITTIG and IRA REMSEN.*

IN the former researches by one of the authors, in conjunction with W. H. Mielck†, there have been described two oxidation-products of piperic acid, viz., *piperonal* and *piperonylic acid*, which stand to one another in the relation of aldehyde and acid; like piperic acid, these compounds contain, in addition to the groups CHO and CO.OH, two oxygen-atoms not associated with hydrogen; the present researches treat of several new reactions of these two substances.

1. *Action of Nascent Hydrogen on Piperonal.*—When an alcoholic solution of piperonal, mixed with a quantity of water insufficient to produce turbidity, is subjected to the action of sodium amalgam at ordinary temperatures for about a week, the precipitate which at first forms ceases to increase; on crystallising this precipitate from alcohol, *hydropiperoïn* is obtained; the filtrate precipitated with water yields *isohydropiperoïn*, much more soluble in alcohol than its isomeride, whilst the mother-liquor of this latter, evaporated until most of the alcohol is driven off, and exhausted with ether, yields *piperonyl alcohol*. The same substances are obtained by the action of solid sodium amalgam and a large excess of boiling water on piperonal, in a flask with an inverted condenser attached. When the melted piperonal has wholly disappeared, hydropiperoïn separates as a yellowish powder, and on allowing the whole to cool, isohydropiperoïn crystallises out in needles. Slightly warm alcohol suffices to separate these two compounds, after pressure on filter-paper, recrystallisation of each from alcohol completing the purification; the piperonyl alcohol is extracted from the alkaline liquid by ether.

Hydropiperoïn, $C_{16}H_{14}O_6$, crystallises in colourless, or slightly yellow, shining, hard prisms, almost insoluble in water and in cold alcohol, and but difficultly soluble in boiling alcohol; it melts at 202°, and is decomposed at a higher temperature; it does not volatilise with the vapour of water, and is not attacked by boiling aqueous potash-ley. A combustion gave numbers agreeing with the formula.

Action of Acetyl Chloride on Hydropiperoïn.—Acetyl chloride does not act readily on hydropiperoïn; a large excess of the chloride heated to its boiling point for 24 hours, gives rise to the following reaction, no solution either of the original hydropiperoïn or of the end-product taking place:

$$\underset{\text{Hydropiperoïn.}}{\begin{array}{c} C_7H_5O_2.CH.OH \\ | \\ C_7H_5O_2.CH.OH \end{array}} + 2(CH_3.COCl) = \underset{\text{Hydropiperoïn chloride.}}{\begin{array}{c} C_7H_5O_2.CHCl \\ | \\ C_7H_5O_2.CHCl \end{array}} + 2(CH_3.CO.OH).$$

* Ann. Chem. Pharm., clix, 129—158. † Ann. Chem. Pharm., clii, 25.

The new product, *hydropiperoïn chloride*, is nearly insoluble in alcohol and water, both cold and boiling; long continued boiling with water decomposes it, hydric chloride being formed; it becomes slightly yellow at 150°, melts at 198°, and decomposes with copious evolution of gas almost at its melting point.

Action of Nitric Acid on Hydropiperoïn. This reaction gives rise to the production of *nitropiperonal*, $C_8H_5(NO_2)O_3$, even in the cold; the same substance is formed by the action of nitric acid on piperonal. It forms large colourless crystals, becoming yellow by the action of light, and is readily soluble in boiling water and in alcohol, but almost insoluble in cold water. It melts at 95·5°, and can be sublimed without decomposition, but does not volatilise with the vapour of water. As previously described,* the production of nitropiperonal is accompanied by that of a crystalline substance, melting at 138°—139°, and volatile with water vapour; by several successive recrystallisations from hot water, this substance loses its volatility with aqueous vapour, and its melting point is lowered to that of nitropiperonal, with which it corresponds in all its properties; probably it is a loose combination of piperonal and nitropiperonal, decomposed by the action of water; or it may be an isomeric nitropiperonal, which becomes transformed into the other modification by the action of hot water.

Isohydropiperoïn, $C_{16}H_{14}O_6$, differs principally from its isomeride, in that it is much more soluble in water and alcohol; even in cold alcohol it is readily soluble, whilst in boiling alcohol it dissolves almost to any extent. It crystallises in colourless needles, and melts first at 135°, but on remelting after solidification, it melts uniformly at 132°, or 3° lower; it cannot be sublimed, nor is it volatile with water vapour. Analyses give numbers agreeing with the formula.

Acetyl chloride acts much more readily on isohydropiperoïn than on its isomeride. In a large excess of acetyl chloride, isohydropiperoïn dissolves readily in the cold, or on slight warming, without production of hydrochloric acid; after some little time, large, colourless, transparent prisms separate from the liquid, no more substance remaining dissolved in the acetyl chloride after 24 hours. Although the aspect of this product differs somewhat from that of the hydropiperoïn chloride obtained from hydropiperoïn, no other difference was discernible. The melting points were the same, viz., 198°, both beginning to show colour at 150°, and decomposing with evolution of gas at the melting point. The analytical numbers in each case agree with those required for the formula $C_{16}H_{12}Cl_2O_4$, so that without doubt the same body is really produced from the two isomeric hydropiperoïns.

Nitric acid acts on isohydropiperoïn just as on its isomeride, pure

* Ann. Chem. Pharm., clii, 47.

nitropiperonal being readily obtainable from the product of the action.

Piperonal, like other aromatic aldehydes, thus appears to yield two isomeric products containing less hydrogen than the corresponding alcohol, and corresponding in some respects to pinacone; Samosadsky,* and later, Rossel,† have observed this with anisic aldehyde, and Ammann ‡ has recently obtained from bitter almond oil a body isomeric with Zinin's hydrobenzoïn.

Piperonyl Alcohol is obtained by evaporation, &c., from the ethereal solution above mentioned, as a thick oily fluid becoming solid on standing over sulphuric acid, and forming by crystallisation from alcohol long colourless crystals melting at 51°; it is not volatile with vapour of water, and may thus be separated from admixed piperonal; in alcohol and ether it dissolves in all proportions, in hot water very easily, but in cold water only with difficulty; it cannot be crystallised from water, separating only as an oil, which becomes solid on standing over sulphuric acid; on distillation it is decomposed, carbon, piperonal, and other substances being produced. Analysis gives numbers agreeing with those required for the formula $C_8H_8O_3$; acetyl chloride and benzoyl chloride gave thick fluid ethers, not further examined for want of material.

Besides the two hydropiperoïns and piperonyl alcohol, the alkaline liquid obtained by the action of sodium amalgam on piperonal contains a small quantity of a brown tarry product soluble in alkalies, and obtained by acidulating and again extracting with ether the liquid from which the piperonyl alcohol had been separated; this substance, however, exists only to a very small amount and cannot be regarded as an essential product of the reaction; altogether, therefore, the action of nascent hydrogen on piperonal appears to be analogous to that of the other aromatic aldehydes, the other two oxygen-atoms contained beside the group CHO being in no way affected.

2. *Action of Nascent Hydrogen on Piperonylic Acid.*—Piperonylic acid was digested with sodium amalgam and water for a fortnight, fresh amalgam being added from time to time as the evolution of hydrogen slackened; hydrochloric acid added to the alkaline liquor precipitated pure unaltered piperonylic acid; the filtrate from this exhausted with ether yielded a small quantity of another acid much more soluble in water, especially when boiling, and crystallising in transparent tables melting at 186°. On repeating this experiment with the piperonylic acid thus regained by precipitation, with the sole difference that from time to time the alkaline liquid produced was neutralised with hydrochloric acid, none of this other acid was obtained

* Zeitchr. für Chem. [2], iii, 678, and iv, 643. † Ann. Chem. Pharm., cli, 25.
‡ Zeitchr. für Chem. [2], vii, 83.

after two weeks' action; probably, therefore, this second acid, the quantity of which was insufficient for analysis, was not a product of the action of nascent hydrogen, but was originally mixed with the piperonylic acid employed.

Hence nascent hydrogen, as in the case of piperonal, does not act on the two oxygen atoms which exist similarly disposed in the two bodies: on the other hand, Foster* finds that piperic acid is capable of taking up two atoms of hydrogen; in order, therefore, to see whether this hydrogen is associated with oxygen (as hydroxyl) in hydropiperic acid, or whether it is taken up by carbon (*i.e.*, whether hydropiperic and piperic acids stand to one another in the same relation as hydrocinnamic and cinnamic acids), hydropiperic ether prepared by Foster's process was treated with acetyl chloride. Neither in the cold nor on heating in a sealed tube at 100° did any action take place; from which it is inferred that the relations of these two oxygen atoms in question are the same in hydropiperic as in piperic acid, in confirmation of which may be cited the behaviour of hydropiperic acid on oxidation described in the first part of these researches.

3. *Action of Barium Hydrate, dilute Hydrochloric Acid, and Water on Piperonylic Acid.*—Ebullition of piperonylic acid with excess of baryta-water for a fortnight gave no decomposition; from the well-known decomposition of the "ketone acids" by this means, with formation of ketones, the absence of an intervening carbon group whose affinities are partly saturated with oxygen may be probably inferred.

When it is heated with dilute hydrochloric acid in a sealed tube at 100°, no reaction ensues, but at 170° the clear and nearly colourless liquid becomes filled with a black substance consisting of unattacked acid and *pure carbon;* no gas whatever is evolved; the aqueous solution filtered from the black deposit was found (by evaporation, extraction with ether, precipitation as lead salt, &c.) to contain, as sole product, *protocatechuic acid.* The reaction, therefore, is—

$$\underset{\text{Piperonylic acid.}}{C_8H_6O_4} = C + \underset{\text{Protocatechuic acid.}}{C_7H_6O_4}.$$

The entire absence of CO and CO_2 in the products of the reaction testifies to the unusual force with which the other two oxygen atoms are combined.

With pure water, at 170°, piperonylic acid undergoes no change, but at 210° the same production of carbon takes place; a considerable quantity of CO_2 is also evolved, arising from the secondary decomposition of the protocatechuic acid into *pyrocatechin* and CO_2; by recrystallisation from toluene, pyrocatechin was obtained in a perfectly pure

* Ann. Chem. Pharm., cxxiv, 115.

state (it is noticeable that by recrystallisation from this menstruum, a much cleaner and purer product is obtained than by any other means heretofore described): pyrocatechin from the above reaction as well as from other sources, thus purified, melted at 102°, whereas other observers have given a higher melting point (111° to 112°); from the perfect identity between the body thus obtained from piperonylic acid and pure pyrocatechin, an analysis was considered superfluous.

4. *Action of Phosphoric Chloride on Piperonal.*—When these two bodies in molecular proportions are brought in contact, action ensues in the cold, the mixture becoming hot and fluid; phosphorus oxychloride is formed, together with an oily substance distilling between 230° and 240°; this does not solidify on standing, cannot be distilled without decomposition, and is decomposed on standing in contact with water. Although this substance was not obtained pure, it was doubtless *piperonal chloride*, $C_8H_6O_2Cl_2$; benzol chloride, $C_6H_5.CHCl_2$, and anisol chloride according to Henry, show analogous properties.

When one molecule of piperonal and three of phosphoric chloride, act on one another, the same reaction ensues; but on warming again after the completion of this first stage, a new reaction sets in, gaseous hydrogen chloride being evolved; phosphorus chloride and phosphorus oxychloride distil over on heating, leaving behind an oily liquid boiling with decomposition at about 280°. When this liquid is placed in a damp atmosphere, a cloud of hydrogen chloride is formed and crystals are produced on the side of the vessel: in cold water no action takes place at first, but in a short time decomposition ensues, hydrogen chloride being evolved, and a mass of crystals formed; these cannot be recrystallised from alcohol or from water, as on warming carbonic and hydrochloric acids are produced; but on dissolving them in alcohol, and adding water till turbidity is produced, long shining colourless needles are obtained; from toluene also this substance can be procured in crystals. The substance thus obtained in crystals from alcohol or from toluene, and the original crystalline mass, alike melted at 90°. The portion purified by treatment with alcohol and water, and dried in vacuo over sulphuric acid, yielded numbers intermediate between those required for the formulæ $C_8H_4Cl_2O_3$ and $C_8H_4Cl_2O_3 + H_2O$; probably, therefore, the compound produced is *hydrate of dichloropiperonal*, analogous to chloralhydrate, part of the water being lost on drying in vacuo, the reactions being—

$$\underset{\text{Piperonal.}}{C_7H_5O_2.CHO} + PCl_5 = \underset{\text{Piperonal chloride.}}{C_7H_5O_2.CHCl_2} + POCl_3.$$

$$\underset{\text{Piperonal chloride.}}{C_7H_5O_2.CHCl_2} + 2PCl_5 = \underset{\text{Dichloropiperonal chloride.}}{C_7H_3Cl_2O_2.CHCl_2} + 2PCl_3 + 2HCl.$$

$$\underset{\text{Dichloropiperonal chloride.}}{C_7H_3Cl_2O_2.CHCl_2} + H_2O = \underset{\text{Dichloropiperonal.}}{C_7H_3Cl_2O_2.COH} + 2HCl,$$

the last formed substance then uniting with water to form a hydrate. Hence phosphoric chloride does not act on the oxygen-atoms contained in piperonal otherwise than on the aldehyde group CHO.

5. *Action of Hot Water on Dichloropiperonal.*—As above stated, this reaction gives rise to the production of CO_2 and HCl; a body crystallisable from water, alcohol, and ether, and containing no chlorine, is simultaneously produced; to get this in the pure state, it is advantageous to exclude air during the action of the water, and to employ toluene as a medium for recrystallisation. On analysis, this body gives numbers agreeing with the formula $C_7H_6O_3$ formed by the reaction $C_8H_4Cl_2O_3 + 2H_2O = C_7H_6O_3 + CO_2 + 2HCl$; it melts at 150°, and is decomposed at a temperature very little higher; its aqueous solution gives an intense and pure green colour with a drop of ferric chloride solution; further addition of a trace of soda-solution gives at first a violet, and on adding more soda, a beautiful red coloration. The aqueous solution has a weak acid reaction, but ether takes up the substance from a solution supersaturated with sodium carbonate. Its production from an aldehyde renders it probable that the group CHO is retained: in fact it reduces ammoniacal silver solutions; and although no crystalline compound with alkaline bisulphites has been obtained, yet probably such a compound exists, as ether fails to dissolve the substance from a solution shaken with sodio-hydric sulphite. From its properties, mode of formation, and connection with protocatechuic acid, it is without doubt *the aldehyde of this acid.* The production of this acid could not indeed be verified by oxidation, either with nitric acid, permanganate, or chromate and sulphuric acid; but by fusion with potassium hydrate, this oxidising reaction ensues perfectly, and without formation of secondary products, hydrogen being evolved. The acid obtained by this process melted after purification at 199°, and gave numbers agreeing with the formula $C_7H_6O_4 + H_2O$; it also gave the qualitative iron reactions (both with the free acid and its barium salt) for protocatechuic acid.

6. *Action of Phosphoric Chloride on Piperonylic Acid.*—This action should give rise to the following series of products:—

(1) $C_8H_6O_4 + PCl_5 = C_8H_5O_3.Cl + POCl_3 + HCl.$
(2) $C_8H_5O_3Cl + 2PCl_5 = C_8H_3Cl_2O_3Cl + 2PCl_3 + 2HCl.$
(3) $C_8H_3Cl_2O_3Cl + H_2O = C_8H_4Cl_2O_4 + HCl.$
(4) $C_8H_4Cl_2O_4 + 2H_2O = C_7H_6O_4 + 2HCl + CO_2.$

whereby successively there are produced—(1) *Piperonylic chloride,* (2) *Dichloropiperonyl chloride,* (3) *Dichloropiperonylic acid,* and (4) *Protocatechuic acid.*

On heating one molecule of piperonylic acid with three of phosphoric chloride, there are produced HCl, PCl_3, and $POCl_3$, as required by equations 1 and 2, and a nearly colourless non-solidifying oil of high boiling point, which soon decomposes with cold water, giving hydrochloric acid and an acid containing chlorine, as per equation 3; lastly, this acid heated with water, gives a vigorous effervescence of carbonic anhydride, and forms a solution containing hydrochloric and protocatechuic acids, without a trace of bye-products, the protocatechuic acid thus obtained being chemically pure, as by equation 4. It was not found possible to isolate any of the intermediate products in a state pure enough for analysis; by the action of cold water, as above mentioned, a chlorinated acid was formed; this was evidently a mixture, as it gave the reactions of protocatechuic acid: the percentage of chlorine agrees with that required for an acid which would have the constitution of dichloropiperonylic acid where one Cl-atom was replaced by hydroxyl, or $C_8H_5ClO_5$. The carbon found, however, is upwards of 4 per cent. in excess of that required by this formula.

7. *Conclusions.*—In the first part of these researches, the view was promulgated that piperonal contains two oxygen-atoms connected together in a manner analogous to that of those in quinone, *i.e.*, that its formula is—

$$C_6H_3\left\{\begin{array}{l}O_2''\\CH_2.CHO\end{array}\right., \text{ or } C_6H_2\left\{\begin{array}{l}O_2'',\\CH_2\\CHO.\end{array}\right.$$

The results just obtained completely contradict this view: out of the numerous other constitutional formulæ that might be ascribed, only one fulfils the conditions required by these reactions, viz.:

Piperonal.

$$C_6H_3\left\{\begin{array}{l}O\\O\\CHO\end{array}\right.\!\!>CH_2.$$

Piperonylic acid.

$$C_6H_3\left\{\begin{array}{l}O\\O\\CO.OH.\end{array}\right.\!\!>CH_2$$

where piperonal is the methylene-ether of protocatechuic aldehyde. This view explains the action of nascent hydrogen on the aldehyde and acid, as in the first only the group CHO can be affected, and in the second no action at all can ensue. Baryta-water does not affect phenol-ethers, and would have no action on this acid; under pressure at high temperatures the attraction of the two oxygen-atoms connected with the benzol residue for the hydrogen of the methylene group, would become so powerful as to break up that group, forming hydroxyl and eliminating carbon: hence the action of water and dilute hydrochloric acid. Lastly, Henry has shown* that phosphoric chloride

* Deut. chem. Ges. Ber., ii, 710; iii, 704. Ann. Chem. Pharm., clvi, 174.

cannot eliminate oxygen which is simultaneously united with two carbon groups.

$$C_6H_3\left\{\begin{matrix} O \\ O \\ CHCl_2 \end{matrix}\right\}CH_2 \quad \text{and} \quad C_6H_3\left\{\begin{matrix} O \\ O \\ CO.Cl \end{matrix}\right\}CH_2,$$

Piperonal chloride. Piperonyl chloride.

which are the first products of the action of PCl_5, can lose no more oxygen by the action of this reagent; any further action can only replace hydrogen by chlorine, yielding—

$$C_6H_3\left\{\begin{matrix} O \\ O \\ CHCl_2 \end{matrix}\right\}CCl_2 \quad \text{and} \quad C_6H_3\left\{\begin{matrix} O \\ O \\ COCl \end{matrix}\right\}CCl_2$$

Dichloropiperonal chloride. Dichloropiperonyl chloride

which must be exceptionally unstable, the chlorine last put in being analogous to that of carbonyl chloride $COCl_2$. These compounds in presence of water, must exchange their Cl_2 for O, and the bodies—

$$C_6H_3\left\{\begin{matrix} O \\ O \\ CHCl_2 \end{matrix}\right\}CO \quad \text{and} \quad C_6H_3\left\{\begin{matrix} O \\ O \\ COCl \end{matrix}\right\}CO$$

thus produced must split up in presence of water, with formation of protocatechuic aldehyde and acid respectively.

Attempts to synthesize methylene-protocatechuic acid (piperonylic acid) are in progress.

C. R. A. W.

On Crystallised Aconitine. By H. Duquesnel.*

Hitherto the term aconitine has been applied to several substances varying in therapeutical value with the source from which they are derived; the author applies the term *crystallised aconitine* to the active principle of the *Aconitum Napellus* obtained by the following process:—

Selected roots are pulverised and mixed with $\frac{1}{100}$ part of tartaric acid, and the whole is exhausted with strong alcohol; the extract obtained is distilled out of contact with air, and at a temperature not exceeding 60°, and the residue is taken up with water to separate fatty and resinous bodies. The aqueous solution of impure aconitine tartrate thus obtained is treated with ether to remove colouring matters, precipitated by an alkaline bicarbonate, and again treated with ether which dissolves the alkaloïd; from this solution the base is obtained in crystals by evaporation, after addition of light petroleum oil, the

* Compt. rend., lxxiii, 207.

crystals being colourless, rhombic, or hexagonal tables, having the composition $C_{27}H_{40}NO_{10}$.*

Neither the alkaloïd nor its salts with mineral acids are affected by a temperature of 100° or lower, either in the dry state or in contact with water; but at 100° in contact with air and its own peculiar extractive liquor, it partly or wholly disappears. The author regards it as a glucoside, and considers that this view explains the spontaneous deterioration of various pharmaceutical preparations of aconite on keeping; it is almost insoluble in water, but readily soluble in dilute acids, even in carbonic acid solution; it is not volatile at 100°, but at 130° it begins to decompose, and, apparently, to volatilise. It is soluble in ether, alcohol, benzene, and especially in chloroform; insoluble in glycerin and in petroleum oils, both light and heavy. It rotates the plane of polarisation to the left, and is amorphous when obtained by precipitation of its salts by alkalies; in this condition it contains water of hydration, which is lost at 100°, without change of appearance; it has a feeble alkaline reaction.

Phosphoric acid, tannin, potassio-mercuric iodide, and iodized potassium iodide, are the most sensitive reagents for aconitine.

C. R. A. W.

Preparation of Creatinine Hydrochloride from Urine. By R. MALY.†

A FEW litres of human urine are evaporated to about one-third of the original volume, and the liquid, after being decanted from the salts which crystallise out, is precipitated with lead acetate. The filtrate is freed from lead by sodium carbonate or sulphuretted hydrogen, and after having been neutralised, either with acetic acid or sodium carbonate, precipitated with mercuric chloride. The precipitate, a combination of creatinine with the mercury salt, is decomposed under water with sulphuretted hydrogen, and the liquid, after treatment with animal charcoal, is evaporated. On crystallising the crystalline residue once or twice from alcohol, pure creatinine hydrochloride is obtained in white crusts or hard shining prisms. The same results were obtained with horses' urine.

C. S.

On the Fatty Constituent of Beer-Yeast. By AUGUST VOGEL‡.

THE author, some time since, indicated the existence in beer-extract of a saponifiable fat, to the extent of 0·16 per 100 parts of the dry extract.

* $C_{54}H_{40}NO_2$ in the original (C = 6, O = 8), probably a misprint for O_{20}, which is required by the numbers given.—C. R. A. W.

† Ann. Chem. Pharm, clix, 279—280. ‡ N. Repert. Pharm., xx, 326—335.

New determinations gave 0·094 gram fat per litre of beer, corresponding in the particular case to 0·15 per cent. of the dry extract.

Further, the bottom-yeast, produced in the course of brewing, was examined for fat; the yeast was allowed to stand for some time, in order to separate the water as much as possible, before proceeding to the exhaustion of the pasty yeast by means of ether. No exact number can be given, but from a litre of yeast in a pasty condition, about 0·2 to 0·3 gram of a fatty oil of yellowish-green colour was obtained.

It was thought to be of interest to compare this fat from yeast with the fat which cereals contain in not inappreciable quantity. It was compared with the fat obtained from barley. Both fats had a yellowish-green colour and a peculiar taste and smell. The fat from yeast is liquid at ordinary temperatures; at $-2°$ the whole mass becomes gelatinous, while grains of solid fat separate. It has a specific gravity of 0·901; the fat from barley has a specific gravity = 0·892.

The oil from yeast is said to boil between 198° and 200°, and to decompose above 300° with development of irritating vapours of acrolein. This oil does not appear to have been analysed or examined chemically.

The yeast which had been treated with ether in order to separate the fat, showed a sensible diminution in its activity as a ferment after this treatment; but this loss of activity is not clearly due to the removal of the fat, as the last portions of the ether cannot be removed from the yeast without the application of heat, which would interfere with the examination of its activity.

W. H. D.

Physiological Chemistry.

On the Question of the Excretion of the Nitrogen of the Albuminoïds Decomposed in the Body. By J. Seegen.*

From some experiments which he performed, Seegen, in opposition to Voit, came to the conclusion that the whole of the nitrogen from the albuminous substances decomposed in the body was not excreted in the urine as urea, but that part of it was excreted in some other way, as by the skin and lungs. The experiments on which the opinions of both observers were founded were performed on dogs which were fed on a weighed amount of horseflesh carefully freed from fat and tendon. These were kept in cages with zinc floors sloping towards the middle, so that any urine passed in the cage could be collected in a vessel

* Wien. Akad. Ber., lxiii, Abt. ii, 11—43.

below. Besides this, they were trained to make water into a vessel which was held beneath them from time to time. Seegen collected their water in this vessel two or three times in the 24 hours, and did so once every morning just before weighing the animal, so that the bladder should be empty at the commencement of each day of experiment, and the urine of one day not retained in the bladder and voided in the next. A certain amount of the urine was generally passed in the cage. In order to discover the cause of the discrepancy in their results, Voit and he undertook some experiments together, each collecting the urine of a dog after his own manner.

Voit's method consisted in causing the animal to micturate into a vessel every two hours or oftener during the day, and making it do so several times in the course of the ten or fifteen minutes before weighing it, so that the bladder should be completely emptied. The result of an experiment lasting ten days, during which the urine was on some days collected in the cage, and on others in a vessel by Voit's method, showed the amount of nitrogen excreted to be 2·5 per cent. less than that ingested. When only those days were reckoned on which the urine was collected by Voit's method, the deficit was merely 1 per cent., and if the increase in the weight of the animal were reckoned as muscle, there would be no deficiency at all, but an overplus of 4 per cent.

By Voit's method also the amount of urine and urea excreted was greater, and the variations from day to day were found to be less than by Seegen's. The smaller variation was probably due to the bladder being more thoroughly emptied at the beginning of each day. The smaller amount of urine and urea obtained by Seegen's method, Voit thinks to be due to loss through imperfect collection, and he thus explains the deficit formerly found by Seegen. This explanation is not allowed by the latter observer, who believes that the greater quantity of urine obtained by Voit's method is simply due to the more frequent micturition causing increased secretion, as Knapp had found it to have this effect.

In order to determine whether or not the deficit he had found could be due to loss of urine, he made several experiments, in conjunction with Voit, Henry, and Schneider, by squirting a given quantity of urine and of solutions of grape-sugar or salt on the floor of the cage, collecting it in a vessel beneath, and determining the loss. These experiments, which have not been correctly described by Voit, showed that even when the fluid was poured on the floor of the cage, under the most unfavourable circumstances, a part of the water was lost, but the loss of solids was not more than 4 to 5 per cent., and, therefore, the deficit of nitrogen amounting to 7—22 per cent., found by Seegen in his previous experiments, could not be due to the loss of urine in collecting, as Voit supposed it was.

In a later series of experiments, Seegen found that the amount of water excreted by the kidneys had little influence over the excretion of nitrogen, the greatest amount of nitrogen sometimes being excreted with the smallest quantity of water. Increased ingestion of water not only increases the amount of urine, but nearly the whole of the extra amount taken in is excreted by the kidneys.

The excretion of water from the lungs and skin is independent of the amount of water ingested. When the air contains much moisture, not only is no water given off by the lungs and skin, but some is taken into the organism through them. The largest amount of nitrogen was excreted by the urine on those days when there was no water excreted by the lungs.

Only on 5—6 of the 60 days during which the experiments were made, was the whole of the nitrogen which was reckoned to be ingested, excreted in the urine, showing that a partial excretion of nitrogen by the lungs takes place as a rule. This agrees with the experiments of Regnault and Reiset, who found an absolute deficiency of nitrogen only in one case, and a more or less considerable excretion of nitrogen in 10 out of 12 experiments on respiration. The objections made by Pettenkofer and Voit to the accuracy of these experiments are refuted by Regnault in a letter which Seegen quotes. The amount of nitrogen excreted during the whole time the experiments lasted, was 3·3 per cent. greater than that ingested. This overplus was not equally distributed over the whole time, but was especially marked during five days, when it was 22 per cent.

As the excretion during the preceding days had not been less than usual, no retention in the body could be suspected; the body-weight remaining the same, the only explanation of this overplus was that the flesh eaten on these days really contained a larger amount of nitrogen than that given by the mode of calculation employed by himself and Voit.

A research by Toldt and Novak in Schneider's laboratory proved the truth of this explanation. This showed that the total nitrogen of the meat was not obtained as ammonia by combustion with soda-lime. The amount of nitrogen varied in different horses and in different muscles of the same horse. The nitrogen from the muscles of one horse was 3·5 per cent., and from another 3·9 per cent. That from different muscles in the same horse varied from 3·78 per cent. to 3·97 per cent. In dogs the variation was still greater, the nitrogen from different muscles in one animal varying from 3·52 to 4·31 per cent.

In Toldt's experiments there appeared to be only a moderate deficiency in the nitrogen excreted in the urine when the nitrogen in the meat ingested was calculated at 3·4 per cent., but an actual analysis of the nitrogen contained in it showed that the deficiency was really 11 to 19 per cent.

As Voit in his experiments assumed the nitrogen content of meat to be 3·4 per cent. and constant, while in reality it varies so much, the law which he founded on them that the whole nitrogen ingested appears again in the urine and fæces, has no sufficient foundation.

T. L. B.

On Tissue-change in Phosphorus Poisoning. By K. Voit.*

In this interesting paper Voit seeks to discover the causes of the fatty degeneration of organs which occur so frequently in disease, by means of experiments on the mode of its production in cases of poisoning by phosphorus. The fat which then appears to take the place of the tissues of which the organs when in a state of health are composed, might be due to three causes—1st. It might be derived from the fat in the food. 2nd. It might have been brought into the organs from other parts of the body which usually contain fat, such as the subcutaneous cellular tissue. 3rd. It might be produced in the cells of the organ itself by albuminous bodies contained in them splitting up and yielding fat and bodies containing nitrogen. In the latter case it is possible that the amount of albumin decomposed, and of fat formed in the cells, may be quite normal, and that its presence in unwonted quantities may be simply due to its not being oxidised. In this case the nitrogenous products of the transformation of albumin, such as urea, will not be changed in quantity, but the oxygen used in the body will be less. It is also possible that more albumin than usual may be decomposed, and especially that which forms an essential part of the structure of the cells themselves, so that they become atrophied, and the tissues disorganised. In this case the urea or other products of the albumin will be increased. The oxygen consumed may remain unaltered, or be less.

By giving phosphorus to dogs which had been deprived of food for several days, Voit and Bauer found that the ordinary symptoms of phosphorus poisoning and fatty degeneration of all the organs were produced.

The fat here could not have come from the food, for the animals got none; nor from other parts of the body, for that had all disappeared, and the animals had become emaciated before the phosphorus was administered, and it must therefore have been produced by the decomposition of albumin in the organs themselves.

On placing one of these dogs in Voit's respiration apparatus, they found that, after giving phosphorus, there was a diminution of 47 per cent. in the CO_2 excreted, and of 45 per cent. in the O absorbed. At the same time they found that the amount of urea excreted, which had been constant for several days before giving phosphorus, rose after its

* N. Rep. Pharm., xx, 340—349.

administration, and became greater as the symptoms of poisoning grew more intense.

These facts show that in phosphorus poisoning the fatty degeneration of organs is due both to the diminished oxidation of fat, and to its increased production from the transformation of albumin. They also show that the transformation of albumin is independent of the supply of oxygen, and that it is not so much albumin itself, as the products of its decomposition, which undergoes oxidation. When oxygen is wanting for this purpose, these products may accumulate to a certain extent in the body.

Schultzen and Riess found that, in slight cases of phosphorus poisoning in man, the amount of urea was increased; but in severe cases it sank to a minimum; and abnormal nitrogenous products, especially peptone-like bodies, insoluble in alcohol, appeared in great quantity, along with a considerable amount of sarcolactic acid. In dogs the urea was invariably increased, and no abnormal products were found in the urine, except a little sarcolactic acid in fatal cases.

Voit and Bauer confirm this latter statement. They looked in vain for leucine and tyrosine in the urine of the poisoned dogs, although these substances occur in abundance in the urine of persons suffering from acute atrophy of the liver, a disease which phosphorus poisoning nearly resembles. They found them, however, in the liver, heart, and blood of the dogs. The nitrogenous products of the decomposition of albumin are therefore converted into urea in all cases in the dog, and in slighter cases of phosphorus poisoning in man. In severe cases in man this decomposition is imperfect, and the higher products of decomposition are excreted. It is highly probable that leucine, and, perhaps, tyrosine, belongs to the first products of the decomposition of albumin.

Schultzen and Rencké have found that leucine is converted in the body into urea, and as leucine and tyrosine are found in the organs, though not in the urine of poisoned dogs, it is possible that they become changed in the body.

Voit thinks that the greater rapidity of degeneration in acute atrophy of the liver, is the chief difference between this disease and cases of phosphorus poisoning. As in fatty degeneration the fat is simply that which has been normally formed in the part, but either not oxidised, or formed in too great quantity, it is difficult to say when the process ceases to be physiological and becomes pathological, and it would be convenient to have names for the different stages. At first the fat will be produced in normal quantity from the store of circulating albumin, afterwards, as in hunger, from the more firmly combined albumin in the organs, and lastly from that albumin which is essential to the constitution of the cells, and whose removal causes their disorganisation and the destruction of the organs which they compose. T. L. B.

On the Physiological Action of Crystallised Aconitine. By MM. GRÉHAUT and DUQUESNEL.*

ONE twentieth of a milligram of aconitine, dissolved in a thousand times its weight of water ($\frac{1}{20}$ cubic centimetre) was injected under the skin of the back of a frog; thirty minutes afterwards the sciatic nerve had completely lost its motricity, though the muscles of the thigh contracted when stimulated by an induced current, and the heart beat regularly.

The gastrocnemius muscles of a frog, with the adherent sciatic nerves, were detached and placed in a solution of $\frac{1}{5}$ milligram of aconitine in one cubic centimetre (1 part in 5,000), so that in one case the nerve was immersed and the muscle not, and in the other, the muscle was covered with the solution, but the nerve not subjected to its action; after some time, the nerve of the first preparation had completely lost its excitability, whilst that of the second caused the muscle to contract whenever excited.

One of the legs of a frog was tied so as to arrest circulation, and the frog then poisoned. All the motor nerves which received the poisoned blood lost their physiological properties, whilst those of the preserved limb remained excitable.

From these results it appears that small doses of aconitine are analogous in physiological results to curarine, destroying the motor power of nerves. A dose of one milligram of aconitine, however, injected into a frog (twenty times as much as that used in the first experiment) completely arrested the contraction of the ventricles of the heart, the auricles alone contracting feebly; the excitability of the motor nerves continued for a long time in this case, and the animal continually moved spontaneously or convulsively. By microscopic examination of another frog similarly treated, it was found that in one minute and a half, the arterial circulation was much slackened, and in three minutes had completely ceased; the nerves did not lose their motricity, because, through the cessation of circulation, they did not come in contact with the poison.

In mammalia, the effects of the poison show themselves more rapidly, and are more difficult to analyse; a milligram of aconitine injected into a rabbit in which artificial respiration was kept up, was found, after half an hour, to prevent the sciatic nerve from producing contraction of the muscles, although these had preserved their contractility.

C. R. A. W.

* Compt. rend., lxxiii, 209.

On the Mucin of the Submaxillary Gland. By J. OBOLENSKY.*

THE paper is a contribution to the chemistry of the as yet imperfectly known substance mucin, first obtained by Städeler from the salivary glands.

Mucin was obtained in the following manner:—The salivary glands of the ox were cleaned as much as possible, and finely rubbed down with pounded glass. The mass was placed in water and allowed to stand over night, then filtered, the residue being again treated in the same manner. The filtrate was precipitated by excess of acetic acid, the precipitate well washed with water, and a little acetic acid, afterwards with warm alcohol, and then dried. This substance, insoluble in acetic acid, is obtained only from the submaxillary gland, the parotid yielding only albuminoïds (globulin). The glands contain none of the substance described by Miescher as nuclein.

Dry mucin gives 2·44 p. c. of pure ash, of which 1·64 parts are soluble in water, the rest in hydrochloric acid. Mucin contains no sulphur. The amount of phosphoric acid (1·06—1·07 p. c.) agrees with the quantity of ash. Mucin free from ash has a composition (the mean of two analyses) 52·2 C., 7·18 H., 11·87 N., 28·75 O. This agrees very nearly with Scherer's analysis of mucin from a cystic fluid, viz., 52 C., 7·0 H., 12·6 N., 28·2 O. It differs from Eichwald's formula chiefly in the amount of nitrogen (Eichwald's formula = 48·9 C., 6·8 H., 8·5 N., 35·8 O).

Freshly precipitated and moist mucin swells readily in water, is easily soluble in lime- and baryta-water, not precipitated by tannic acid, ferric chloride, or mercuric chloride. It is soluble in concentrated hydrochloric and nitric acid, also in sodium carbonate. When mucin is treated with hot alcohol and dried on the water-bath, it scarcely swells in water, and is very slowly soluble in lime- or baryta-water, or soda-solution. The solutions behave like the former in regard to the above-mentioned reagents.

Dried and pulverised mucin, heated for 25 minutes with dilute sulphuric acid, is partly dissolved, and gives with excess of caustic soda and copper sulphate a rich precipitate of cuprous oxide. If it be heated for a longer time, the quantity of reducing agent diminishes, and ultimately disappears. This fact, and the insolubility of the reducing agent in absolute alcohol, show that it is not identical either with grape-sugar or milk sugar.

D. F.

* Med.-chem. Unters., 1871, 590—593.

On the Artificial Production of Calcareous Substances, such as are found in the Organism. By M. HARTING.*

M. HARTING announces in a preliminary note that he has succeeded in imitating the greater number of the forms which carbonate of lime assumes in the organism, such as biliary and other concretions, the various forms of otolites, pearls, coccolites, the spicules of the alcyonaria, the various substances which form the shells of molluscs, the calcification of cartilage, the calcareous couches of the scales of osseous fishes, &c. He has not yet succeeded in imitating the pieces of the tegumentary skeleton of the echinodermata, or the osseous substance of the vertebrate skeleton. His method of procedure was to imitate nature in regard to the length of the process. He formed the calcareous combinations in organic fluids by means of double decomposition, retarded by very slow diffusion. The paper is not yet ready in all its details.

D. F.

Agricultural Chemistry.

On the Nitrous Acid present in the Water and Mud of Irrigation Canals. By CHABRIER.†

THE author's analyses of mud deposited by irrigation canals gave the following results. The figures represent milligrams per kilogram :—

No.	Description of deposit.	Moisture.	Nitrous acid.	Nitric acid.
1	Argillaceous, from the St. Chamas Canal; had been exposed to air eight months	33600	·72	279·27
2..	Sandy, from sides of same canal, never dried ..	44400	·68	69·20
3..	Ditto, dried at 80°	220	None.	68·13
4..	Ditto, dried by exposure to air in dry weather	660	None.	69·00
5	From mouth of the Boisgelin Canal, a year old	1450	·88	138·80
6	From a branch of the Boisgelin, several years old	45100	10·108	130·87

The argillaceous deposit (No. 1) contains far more nitric acid than the sandy deposit (No. 2) from the same canal. Clay has the property of accumulating nitrous and nitric acids. The author found in 1 kilogram of commercial kaolin 34·973 milligrams of nitrous acid, and 521·46 milligrams of nitric acid. Experiments 3 and 4 show that

* Compt. rend., lxxiii, 361. † Compt. rend., lxxiii, 249—254.

moisture cannot be perfectly expelled without destroying the nitrous acid.

The analyses of canal waters gave the following results. The figures represent milligrams per litre:—

No.	Description of water.	Nitrous acid.	Nitric acid.
1....	Canal of St. Chamas, water taken in January.....	·329	·002
2....	The same, water taken in May	·247	·003
3....	Canal of Boisgelin, water taken in March	·952	2·487
4....	The same, water taken in May	·161	·771
5....	Overflowing of branch of Boisgelin, taken in March	·965	4·023
6....	Another canal, water taken in January	·274	1·923
7....	Canal of Touloutre, water taken in March	·238	·005

The amount of nitrous acid appears to be greatest in winter and spring time, and to diminish towards the summer.

R. W.

Analytical Chemistry.

On the Use of Bromine in Chemical Analysis. By P. Waage.*

The author passes in review the different oxidising agents usually employed, viz., nitric acid, potassic chlorate and hydrochloric acid, and lastly, chlorine. The action of nitric acid, he observes, is but feeble when the acid is used in a dilute state, and even when concentrated it oxidises sulphur but slowly. Most solutions under analysis are rarely quite free from hydrochloric acid (chlorides), and the use of platinum vessels has therefore to be carefully avoided. Nitric acid acts upon filter-paper, the products preventing the complete precipitation of certain metallic oxides. Potassic chlorate necessitates the employment of concentrated hydrochloric acid; and any undecomposed chlorate, especially in dilute solution, can only be removed by introducing into the solutions a large excess of free hydrochloric acid. Chlorine-water is a comparatively weak oxidising agent, as it contains only about $\frac{1}{2}$ p. c. of chlorine. The use of gaseous chlorine, lastly, involves each time the generation of chlorine and the getting ready of a chlorine apparatus. The author recommends, therefore, the more frequent use of bromine, both in qualitative and quantitative analysis, either in the form of pure bromine, or dissolved in water, or in concentrated hydrochloric acid. Bromine-water, ob-

* Zeitschr. f. Anal. Chem., x, 206—209.

tained by shaking up bromine with cold water, contains from 2 to 3 per cent. of bromine; concentrated hydrochloric acid takes up about 13 per cent. We may fix upon any of these three oxidising agents according to the intensity of the oxidising power to be exerted. Excess of bromine can be very easily removed by heat. Bromine, moreover, is without action upon platinum vessels, either in alkaline or acid solutions, free nitric acid excepted, and, when used in the form of bromine-water, or dissolved in hydrochloric acid, does not act upon filter-paper—a great desideratum, whenever precipitates have to be partly oxidised on the filter itself.

Bromine was found to be a useful and powerful solvent for sulphur, magnetic pyrites, copper pyrites, arsenical pyrites, and nickel glance, as well as for precipitated sulphides, for determining either the sulphur or the metals. Sulphur, when shaken up with bromine and water, is speedily converted into hydrobromic and sulphuric acids, provided each sulphur-atom meets with at least 6 atoms of bromine, *i.e.*, 15 parts by weight of bromine require one of sulphur. The whole of the bromine is added at once, in order to avoid loss of sulphur in the shape of sulphur bromide. The pyrites need not be powdered very finely; the action of bromine being very violent, it is advisable to add first a little water to the pieces of pyrites, and then the bromine gradually, and, with repeated shaking, in small quantities at a time.

Bromine-water may conveniently be used for removing sulphuretted hydrogen from solutions. Precipitated metallic sulphides are, for the most part, removed from the filter by a fine jet of water from a wash-bottle, and the last traces are treated on the filter by pouring a little bromine gas or bromine water into the funnel and covering it up with a watch-glass. The sulphides are rapidly oxidised and absorbed by the filter, and can then be washed out.

Bromine does not oxidise in ammoniacal solutions, but liberates nitrogen; ammonia may therefore be used with advantage for removing excess of bromine. The presence of ammoniacal solutions prevents, in some instances, the oxidising action of bromine. The peroxides of nickel, and cobalt, are not precipitated by bromine from solutions containing ammoniacal salts. Ferrous, stannous, and mercurous salts, on the contrary, are readily oxidised by bromine in an acid solution in the presence of ammoniacal salts.

Commercial bromine cannot always be obtained pure, and should be redistilled, if necessary.

W. V.

On the Action of Phosphorus Dissolved in Carbon Disulphide on a Solution of Blue Vitriol. By WERNER SCHMID.*

A CLEAR solution of phosphorus in carbon disulphide, when shaken up with excess of a solution of pure cupric sulphate, yields a filtrate which acts but slightly upon solutions of silver, or upon an acidulated solution of potassic permanganate, thereby showing that it contains only traces of hypophosphite and phosphite. It acts, however, strongly upon litmus, cane-sugar, and ammonic molybdate, owing to the presence of free sulphuric and phosphoric acids.

The spongy voluminous precipitate is washed first with water, then with alcohol, and, lastly, with carbon disulphide, and pressed between bibulous paper. It dissolves only partially in highly-diluted hydrochloric acid. The solution is colourless, and becomes blue by being shaken up with ammonia only in the presence of air. This shows the presence of a cuprous compound. Concentrated hydrochloric acid likewise dissolves the precipitate merely partially, yielding a brownish-yellow solution which turns blue with ammonia in presence of air, and reduces ammonic molybdate to an intensely azure blue solution. The latter is decolorised by nitric acid, and yields a yellow precipitate. On treating with concentrated nitric acid, the spongy precipitate dissolves completely, with evolution of nitric oxide and formation of cupric sulphate and phosphate. Fusion with saltpetre effects the same. Sodic hydrate evolves non-spontaneously inflammable phosphine. It follows from all these observations that the precipitate consists of cuprous oxide, cuprous or cupric sulphide, and phosphide. Minute scales of metallic copper were observed only when the solution of the copper salt was allowed it to float quietly on the phosphorus solution, although no metallic copper could be detected in the precipitate.

W. V.

On the most Important Methods of Determining Arsenic Volumetrically. By E. WAITZ.†

THE author has investigated with great care the different methods for determining arsenious acid, viz., 1st, by means of free iodine; 2nd, by means of dipotassic dichromate; 3rd, by means of potassic permanganate; as well as the method for estimating arsenic acid by means of uranic acetate.

The iodine method depends, as is well known, upon the conversion of arsenious into arsenic acid in alkaline solution. In an acid solution arsenious acid can exist in the presence of iodine or chlorine, and is only partly converted into the higher oxide. The alkali must be in the form of a carbonate, for a caustic alkali combines with the iodine.

* Zeitschr. f. Anal. Chem., x, 205. † Zeitschr. f. Anal. Chem. x, 158—183.

The author's experiments show that normal sodic carbonate fixes iodine, but that the acid carbonate does not; a solution saturated in the cold should be used. This only confirms the previous observations of Fresenius. On employing a standard solution of arsenious acid in hydrochloric acid, the free acid has first to be neutralised by means of caustic soda or acid sodic carbonate. With an excess of this latter salt, good results were obtained.

Experiments made with a view of converting precipitated arsenious sulphide into arsenious acid by the action of an ammoniacal solution of silver nitrate upon the sulphide dissolved in ammonia, as well as by means of freshly precipitated bismuthous hydrate, and of substituting in this manner the trisulphide—which can be obtained in a state of great purity—for the trioxide, were unsuccessful, as the reaction is never quite complete, owing to the formation of sulpho-salts of silver and bismuth.

The method first proposed by Kessler* of determining arsenious acid in an acid solution by means of dipotassic dichromate, and standardising back by means of a ferrous sulphate solution, gave good results. Excess of hydrochloric acid has to be avoided. Kessler succeeded in utilising arsenious sulphide by treating it in a hydrochloric acid solution with mercuric chloride, a saturated solution of which converts the sulphide slowly at the ordinary temperature, more rapidly on the application of a *gentle* heat, into the trioxide. The reaction is over when the mass has become white. The author's experiments show further that the mixture of trisulphide and sulphur which is obtained when a solution of arsenic acid is precipitated with sulphuretted hydrogen, cannot be converted directly into arsenious acid by digestion with mercuric chloride, on account of the dense nature of the precipitate, but that it is readily acted upon, after dissolving out the trisulphide by means of dilute ammonia and reprecipitating with hydrochloric acid.

The oxidation of arsenious into arsenic acid by means of potassic permanganate is never perfect,† and a volumetric method based upon this reaction was found by the author to be most untrustworthy; but by adding excess of permanganate—more than double the amount required according to theory—and standardising back with a solution of ferrous sulphate, very accurate results were obtained.

The volumetric determination of arsenic acid by means of uranic acetate in the presence of free acetic acid and an alkaline acetate, did not yield trustworthy results.

W. V.

* Pogg. Ann., cxviii, 17; and Fres. Zeitschr. für Anal. Chemie, ii, 383.

† Gmelin, Handbuch der Chem., 4th ed., ii, p. 640.

A New Method for Separating Magnesia from Potash and Soda. By H. SCHEERER.*

EVAPORATE the hydrochloric acid solution of the metals nearly to dryness in a platinum crucible; dry, heat gently, then to full redness; treat the residue with water, boil, and filter. Magnesium carbonate is found on the filter—potassium and sodium carbonates in the filtrate. This method is stated to yield good results. Sulphates, however, must not be present.

A. T.

The Separation of Zinc from Nickel. By A. KLAYE and A. DEUS.†

IN consequence of the discrepancies in the results obtained by different processes for the quantitative separation of zinc from nickel, the authors, at the suggestion of Fresenius, undertook the examination of several recognised methods.

Berzelius'.—A solution containing ·1795 grm. of nickel oxide and ·1965 grm. of zinc oxide gave, by this method, ·0069 grm. zinc oxide, soluble in potassa, and nickel equal to ·180 grm. nickel oxide.

Ullgren's.—It is stated that hydrogen, passed over the heated oxide, reduces only nickel oxide, and that ammonium carbonate dissolves zinc oxide only from a mixture of this substance and nickel.

I.	·1725 grm. NiO	+	·1590 grm. ZnO	lost by H	·0487 grm.	
II.	·1597 ,,	,,	·1471	,,	·0508	,,
III.	·1460 ,,	,,	·1345	,,	·0485	,,

the calculated loss for the reduction of the nickel oxide being ·0368, ·0341, and ·3311 respectively, from which it appears that in the first experiment ·0526 of zinc oxide was reduced; in the second, ·0846; and in the third, ·0881 grm.

The residues digested with ammonium carbonate dissolved some nickel as well as the zinc oxide. The solution of III gave ·021 grm. nickel oxide and only ·0597 grm. of zinc oxide, *i.e.*, ·0748 less than the quantity taken, which agrees somewhat with the calculated amount of zinc oxide reduced. The presence of metallic zinc in the residues was confirmed by other observations.

Brunner's.—Cold dilute hydrochloric does not, as stated, dissolve the whole of the zinc sulphide. If warm hydrochloric acid be used, some nickel sulphide dissolves as well as zinc sulphide.

Wöhler's.—·1965 grm. zinc oxide + ·1795 grm. nickel oxide gave, by this method, ·1976 of zinc oxide and ·1813 nickel oxide.

The following results were obtained: (1) By substituting pure

* J. pr. Chem [2], iii, 476. † Zeitschr. Anal. Chem., x, 190.

freshly prepared potassium cyanide for hydrocyanic acid; (2) by weighing the zinc as sulphide. The latter was effected by washing the precipitated zinc sulphide with sulphuretted hydrogen, drying, and heating in a current of hydrogen until its weight remained constant.

I. ·1965 grm. ZnO + ·1795 NiO gave ·1903 ZnO and ·1894 NiO.
II. „ „ „ „ ·1945 „ ·1802 „

Smith and Brunner's.—The following modification of this method is recommended in consequence of some nickel having been found with the zinc precipitated by sulphuretted hydrogen. Add sodium carbonate to the hydrochloric or nitric acid solution of the metals, until there is only a trace of free acid; pass sulphuretted hydrogen until the precipitation of zinc sulphide ceases; add a drop of a very dilute solution of sodium acetate; and again pass sulphuretted hydrogen.

I. ·1965 grm. ZnO + ·1795 NiO gave ·1952 grm. ZnO and ·1795 NiO.
II. ·1965 grm. ZnO + ·1795 NiO gave ·1948 grm. ZnO and ·1788 NiO.

A. T.

Observations made during the Analysis of Commercial Tin. By H. SCHEERER.*

WHEN chlorine is passed over heated metallic tin, there is produced, should the gas be not perfectly dry, in addition to stannic chloride, a small quantity of a white crystalline sublimate having the composition $SnCl_4.3H_2O$. If a very small quantity of water be added to this compound, or it be allowed to deliquesce, sulphuretted hydrogen precipitates the ordinary yellow stannic sulphide; but if it be dissolved in a large quantity of water, a yellowish-brown precipitate is produced by the same reagent. The author attributes this to the formation, by the excess of water, of metastannic chloride, from the solution of which the yellowish-brown metastannic sulphide is precipitated by sulphuretted hydrogen.

Metastannic chloride is also produced when a quantity of water is added to ordinary stannic chloride. This change is prevented by free acid, especially if water be not present in great excess.

On dissolving several quantities of the same sample of tin in *aqua-regia* and subsequently decomposing with sulphuretted hydrogen, stannic sulphide differing in colour was produced, which was also attributed to the formation of variable quantities of meta-stannic sulphide.

* J. pr. Chem. [2], iii, 472.

The yellowish-brown sulphide was analysed with the following results:—

	Dried over sulphuric acid.	Dried at 140°C.
Tin	53·46	59·29
Sulphur	28·76	31·89
Water (by loss)	17·78	8·82
	100·00	100·00

The first analysis indicates the formula $SnS_2.2H_2O$; the second, $SnS_2.H_2O$.

A. T.

Notes on Organic Analysis. By Hugo Schiff.*

1. *Volumetric Estimation of Typical Hydrogen in Ammonia-bases.*—A. W. Hofmann has described† a method of discriminating between the primary, secondary, and tertiary amines, depending on the production of the corresponding iso-nitriles and mustard oils; where this method is not applicable, Hofmann proposes to employ the reaction of the iodides of the alcohol-radicals, pointing out at the same time the disadvantages of this method, viz., that considerable quantities of substance must be used, that mixed products are frequently obtained, and finally that a weight-analysis must be made after purification; a still further disadvantage is that the whole operation must be repeated for each hydrogen-atom.

The author has previously shown that the action of aldehydes on primary and secondary amines is expressible by the general equations:—

$$R'.NH_2 + C_nH_mO = H_2O + R'.NC_nH_m.$$

$$\begin{matrix} R'_2.NH \\ R'_2.NH \end{matrix} + C_nH_mO = H_2O + \left.\begin{matrix} R'_2.N \\ R'_2.N \end{matrix}\right\} C_nH_m.$$

These reactions in many instances occur at the ordinary temperature, or at temperatures but little elevated, so perfectly that the water actually separated differs by only an inappreciable quantity from the theoretical amount. The aldehyde most convenient for quantitative estimation based on this principle, on account of its easy purification, high molecular weight, slight volatility, and comparative unalterability, is *œnanthic aldehyde.* A recent estimation of its specific gravity gives the number 0·8257 at 13°, whence its molecular volume is calculated as 139.

139 vols. of œnanthic aldehyde represent, according to the above equations, *two* atoms of hydrogen in the form of water, or 0·7 c.c.s.

* Ann. Ch. Pharm., clix, 158—168. † Deut. Chem. Ges. Ber., 1870, 767.

represent 0·01 gram of hydrogen; hence if the molecular weight of a base (or a multiple thereof) in centigrams be weighed out, every 0·7 c.c. of œnanthol employed for perfect action represents *one* atom of typical hydrogen; or if 69·5 c.c. of œnanthol are dissolved in benzene to 100 c.c., then each c.c. of the mixture used represents *one* centigram of typical hydrogen.

The mode of analysis is very uniform; into a small test-tube 2 to 4 grams of the base are weighed and dissolved in 2 to 3 times its bulk of benzene; some grams of *fused* calcium chloride in lumps the size of peas are added, and lastly the œnanthol solution is dropped in from a burette divided into $\frac{1}{50}$ c.c.; each drop produces a thick turbidity from the separation of water, which is readily taken up by the calcium chloride on gentle agitation; as soon as no more turbidity is produced the titration is finished.

By this means satisfactory results have been obtained in the titration of amylamine, diamylamine, aniline, toluidine, ethylaniline, naphthylamine, and toluylene-diamine, as for example—

Aniline boiling constantly at 185° to 186°, but containing a small quantity of toluidine.

2·312 grams	required	3·4 c.c. œnanthol	: calculated	3·45 c.c.
2·240	,,	3·25 ,,	,, ,,	3·34 ,,

Hence one molecule = 93 grams represents 1·95 grams of typical hydrogen, instead of 2 as required by theory.

The same reaction may be employed in the approximate analyses of mixtures of bases; by this means it is shown that distillation alone will not suffice for the separation of diethylaniline and ethylaniline, several per cent. of the latter base being retained; this may, however, be separated by addition of œnanthol, as the septene-diethyl-diphenylamine produced does not volatilize at the boiling point of diethylaniline; similarly ethyl-aniline, though of constant boiling point, always retains a little diethylaniline.

It is necessary that *fused* calcium chloride be used, the ordinary spongy substance absorbing some of the base and preventing the complete action of the œnanthol; it is best not to add the calcium chloride at first, but to commence by adding a little œnanthol, which sets free some water; the calcium chloride is then dropped in, and becomes covered with an *aqueous* layer, after which the operation proceeds readily; if the calcium chloride be directly added to the dry benzene solution, its surface is moistened by the benzene, and the absorption of water proceeds much less quickly. A certain amount of turbidity is always produced on adding œnanthol to benzene, even though the latter already contains œnanthol; this appearance is in practice distinguishable from the turbidity caused by the evolution of water.

The behaviour of œnanthol with triamines has been studied only in the case of rosaniline, and the action of amines of the classes $N_2\left\{\begin{matrix}R'''\\H_3\end{matrix}\right.$, and $N_2\left\{\begin{matrix}R''\\R'\\H_3\end{matrix}\right.$, has yet to be investigated; further researches on this and allied subjects are in progress.

2. *A reaction of free Phenol-hydroxyls.*—By comparing the colour reactions given by several benzene derivatives with solution of ferric chloride containing as little free acid as possible, the conclusion is drawn that only those bodies which contain hydroxyl associated with the benzene nucleus are capable of giving colours with this reagent. As even in these cases the substitution of NO_2 for hydrogen appears to prevent the reaction, substances containing nitrogen are left out of consideration.

Violet tints are obtained with phenol, salicylic acid, cresotic acid, salicylic aldehyde, gaultheria oil, saligenin, phenyl-sulphuric acid, &c.

Blue colours with tannin, gallic acid, pyrogallic acid, and many tannin derivatives, *e.g.*, arbutin.

Green tints are obtained with many tannin derivatives, as æsculetin, para-æsculetin.

Red and *violet red* colours with phlorizin, phloretin, tyrosin, nitro-salicylic acid, and some others.

No colour with picric acid, dinitrohydroquinone, dimethyl salicylate, amygdalin, salicin, helicin, diarbutin, acetyl-gallic acid, mandelic acid, the acetyl and benzoyl derivatives of the glucosides of this class of bodies generally, ethyl-salicylol, &c.

When the hydrogen of the hydroxyl is replaced by another group the coloration ceases; thus may be compared *saligenin* with gluco-saligenin (salicin); *salicylol* with ethyl-salicylol, or glycosalicylol (helicin); *æsculetin*, *phlorizin*, and *arbutin*, with their saturated acetyl derivatives; *salicylic acid*, and *gaultheria oil*, with dimethyl salicylate, &c.

The intensity of the colour seems to bear a ratio to the number of free hydroxyl-atoms; thus the previously mentioned violet tint producing bodies contain only *one* hydroxyl, while the deep blue violet and nearly black colours are given by bodies containing *more* than one hydroxyl.

From these considerations conclusions may be drawn as to the structure of certain benzene-derivatives which otherwise might be doubtful; thus phenyl-sulphuric acid is $C_6H_4\left\{\begin{matrix}OH\\SO_2.OH\end{matrix}\right.$, and not $\left.\begin{matrix}H\\C_6H_5\end{matrix}\right\}SO_4$; so gaultheria oil is $C_6H_4\left\{\begin{matrix}OH\\CO.OCH_3\end{matrix}\right.$, and not $C_6H_4\left\{\begin{matrix}OCH_3\\CO.OH\end{matrix}\right.$, which view is confirmed by the absence of colour-reactions with

dimethyl salicylate; similarly the author proposes the following formulæ—

Arbutin.

$$C_6H_4\left\{\begin{array}{l}OH\\O.C_6H_{11}O_5.\end{array}\right.$$

Salicin.

$$C_6H_4\left\{\begin{array}{l}O.C_6H_{11}O_5\\CH_2.OH.\end{array}\right.$$

Æsculetin.

$$C_6H_2\left\{\begin{array}{l}CHO\\C.OH\\C.OH\\OH\end{array}\right.$$

Æsculin.

$$C_6H_2\left\{\begin{array}{l}CHO\\C.OH\\C.OH\\O.C_6H_{11}O_5.\end{array}\right.$$

Paraæsculetin.

$$C_6H_2\left\{\begin{array}{l}(CHO)_3\\OH.\end{array}\right.$$

It is noteworthy that several substances which give colours with aqueous solutions do not in presence of alcohol; large excess of acid is prejudicial, whilst alkalies completely hide the reactions; dilute aqueous solutions answer best.

C. R. A. W.

Valuation of Oil Seeds. By Dr. H. Vohl.*

In a previous paper the author described an apparatus for the estimation of oil in seeds. The results of a number of determinations so made are here given. The average of ten samples of the following seeds is in 100 parts: linseed 27·15, hemp 25·87, poppy 49·4, walnuts 50·06, almonds 52·41, seeds of grapes 17·95.

Further particulars are given on the mode of conducting the extraction. There is also appended a very useful table, showing the specific gravity at 15° of the Canada oil extract for percentages of oil from 0 to 50 of the following seeds: rape, linseed, hemp, poppy, walnut, almonds, grapes.

A. T.

Technical Chemistry.

On Fire-clays. By Carl Bischof.*

In judging of the pyrometrical value of fireclays from the chemical analysis, the author insists that regard should be had:—

1. To the proportion of alumina and fluxes;† and,
2. To the proportion of alumina and silica.

* Dingl. polyt. J., cc, 110—120.

† The oxides of the alkalies and alkaline earthy metals as well as of dyad iron, &c.

The measure for the pyrometrical resistance of a clay is obtained by accurately determining how much alumina exists, together with a certain quantity (1 part) of fluxes, and, at *the same time*, how much silica goes with a certain quantity (likewise 1 part) of alumina. The more alumina a clay contains for every one part of fluxes, the more difficultly fusible is it; on the other hand, the fusibility of a clay at high temperatures increases directly with the quantity of silica which it contains.

Of two clays, *e.g.*, the one containing more alumina and at the same time less silica, must necessarily be the less fusible, whilst the one containing less alumina but more silica,—assuming the physical conditions to be the same, or at least similar,—will undoubtedly turn out to be the more fusible. Of two clays containing the same proportion of alumina to fluxes, the one containing relatively less silica will be found to resist heat better. The reverse holds good. Of two clays having the same proportions of aluminous and silicious constituents, the pyrometrical resistance—with a few well-defined exceptions, which are dependent upon certain external properties of the clays —will be the same.

If among two or more clays sometimes the one sometimes the other proportion prevails, the pyrometrical status may be ascertained by a simple calculation. For the purpose of illustrating these proportions the author takes certain typical clays, the analyses of which are sufficiently well established to allow of deducing mineralogical formula, viz.:—

1. A clay from Saarau, in Lower Silesia, being an average sample of several hundred tons taken out during the year 1863, and representing one of the best known continental fire-clays. The analytical composition is expressed by the formula—

$$16{\cdot}39\ (Al_2O_3,\ 1{\cdot}69\ SiO_3) + RO,$$

or for every 16·39 of alumina we have 1 part of fluxes (RO), and for every 1 part of alumina there is 1·69 of silica. The same clay, when carefully selected, had the chemical composition 19·25 (Al_2O_3, 1·38 SiO_3) + RO, or for every 19·25 of alumina there was 1 part of fluxes. 1 part of alumina requiring only 1·38 of silica. The latter clay undoubtedly constitutes a still better material for resisting high temperatures; for not only has the amount of alumina increased as compared with the fluxes, but likewise in proportion to the silica present in the clay. By dividing the larger with the smaller figure, the author obtains a quotient which represents a very simple standard of the pyrometrical value of a clay as deduced from its chemical analysis, viz., as $\frac{19{\cdot}25}{1{\cdot}38} = 13{\cdot}95$. In like manner he obtains for the larger

average sample of the same clay the quotient $\frac{16 \cdot 39}{1 \cdot 69} = 9 \cdot 70$, and the pyrometrical value of the two clays is expressed by the quotients 9·70 and 13·95.

Bischof fixes in like manner on six other representatives of standard (or typical) clays, viz. :—

Class 2.—An elutriated kaolin from Zettlitz, in Bohemia, representing a naturally pure elutriated porcelain earth. Chemical composition : 12·82 (Al_2O_3, 1·35 SiO_3) + RO ; quotient of pyrometrical value = 9·49.

Class 3.—A normal white clay, from Saarau, rich in silica. Chemical formula (according to E. Richters): 14·15 (Al_2O_3, 5·01 SiO_3) + RO ; quotient = 3·82. A normal clay from Ardennes, Belgium, distinguished by great fatness and plasticity. Chemical composition : 6·86 (AlO_3, 1·63 SiO_3) + RO ; quotient = 4·21.

Compared with the clays of class 2, the proportion of alumina has decreased considerably in the latter, whilst the silica has at the same time increased. Clays of this class are necessarily inferior.

Class 4.—A clay from Mühlheim, near Coblentz (best average sample), used instead of Belgian clays. Chemical composition : 5·96 (Al_2O_3, 1·51 SiO_3) + RO ; quotient = 3·95.

The proportion of alumina to fluxes is less in the latter, compared with the Belgian clay ; the proportional amount of silica, however, has likewise decreased. A glance at the respective quotients leaves no doubt as to the inferior pyrometrical value of the Rhenish clay.

Class 5.—Potter's earth from Grünstadt, a representative of kaolin-like clays from secondary formations. Chemical composition : 3·65 (Al_2O_3, 1·54 SiO_3) + RO ; quotient, 2·37.

Class 6.—A clay from Oberkaufungen, near Cassel. Chemical composition : 4·41 (Al_2O_3, 2·37 SiO_3) + RO ; quotient = 1·86.

Class 7.—Clay from Lower Pleis, on the river Sieg. A representative of ordinary fire-clays from brown-coal mines. Chemical composition : 3·89 (Al_2O_3, 2·37 SiO_3) + RO ; quotient = 1·06.

A glance at the different quotients shows :—

1. That the pyrometrical resistance decreases directly as the quotients decrease. The ratio of decrease in inferior clays is slight ; in the better class fire-clays it goes on progressively.

2. The kaolin of Saarau, in class 3, forms the only remarkable exception to this law, for the calculated quotient assigns to the clay a position two stages lower in the scale. In order to clear up this apparent contradiction, the author repeated the pyrometrical determinations most carefully by forming this Saarau clay and the Mühlheim clay into equally large pyramids, before he exposed them to a heat capable of melting wrought iron. The former again resisted this heat better than the latter. On increasing the temperature to the

melting point of platinum (platinum foil was inclosed within a capsule of alumina and melted up into a ball) the Saarau clay became glased, but the edges of the pyramid were left intact and the inside remained compact, only isolated blisters being discernable by means of a lens. The Mühlheim clay was covered superficially with a molten yellow, somewhat frothy mass; the edges of the pyramid appeared rounded off, and the interior was entirely filled with large blisters. By increasing the temperature above the melting point of platinum—as high in fact as the experimental crucible withstood—both clays became softened: the Saarau clay formed a lustrous mass, filled with fine blisters, yet of unmistakeably dense structure, whilst the Mühlheim clay consisted merely of one porous mass throughout. The former clay was therefore the less fusible of the two. This result was obtained, however, by employing both clays, so to speak, in their natural condition, merely roughly crushed. It was found that the Saarau clay contained coarse grains of quartz as large as a pin's head, whilst the Mühlheim clay consisted of an impalpable powder. By grinding the former to an equally impalpable mass, forming the clays into small pyramids and exposing them to a heat required to melt platinum, the Saarau clay melted into a ball, whilst the Mühlheim clay showed still the pyramidal form, although the edges were melted away considerably. On repeating the experiment with pyramids of uncrushed as well as finely crushed Saarau clay, the former retained its sharp edges, whilst the etches of the latter had melted away.

The known fact that coarse pieces of quartz, when mixed with clay, impart to it invariably a relatively higher power for resisting heat—in this special case, in fact, an absolutely higher power—than when the same quartz, in the form of fine powder, is impounded with the clay, is amply verified by these experiments. Pyrometrical testings assign to the raw Saarau clay a higher position than is borne out by chemical analysis; as soon, however, as the clay is finely powdered, its power of resisting heat sinks below that of the normal clay of the next following class, and is in harmony with the results of the analysis. Similar anomalies were observed by E. Richters.

3. Again, the normal clays of the first two divisions show how clays of very similar chemical composition may exhibit essentially different pyrometrical resistance. Bischof ascribes this difference to the different conditions of aggregation.

Judging, also, from a series of analyses of fire-clays, by E. Richters, which the author quotes, it would appear that the quotient does not always express the pyrometrical value of a clay, but that other conditions—among which, especially, the state of aggregation, the nature of the siliceous constituents, *e.g.*, whether present in the form of coarse or fine sand, quartz, &c.—have to be taken into consideration.

In a second paper,* Bischof explains that the relation between the fluxes and the silica is entirely different from that of the alumina to the fluxes, as well as to the silica. An increment of alumina in silicious clays, such as are most commonly found in nature, at once raises their pyrometrical resisting power, whilst an additional amount of fluxes brings it down, the action of the two being diametrically opposed; it follows, therefore, that when the alumina is once taken as unit of comparison, the relation existing between the silica and the fluxes cannot at the same time be brought into correlation with it. The author insists that the quantity of fluxes as well as of silica should be determined analytically with the greatest accuracy, on account of the importance which attaches to the proportion between either of them to the alumina, rather than to the proportion between themselves, and he compares two clays from the coal formation near Saarbrück, one being found more pure in a pit near Wellesweiler, the other of less purity, *i.e.*, contaminated with more sand, especially more oxide of iron and magnesia, in the pit of Duttweiler, near Saarbrück. The former variety is far more difficultly fusible than the latter. We quote the results of the chemical analysis in a tabular form, I representing the clay from Wellesweiler; II the Duttweiler clay:—

	SiO_3 and Sand.		Al_2O_3.	FeO.	CaO.	Mgo.	K_2O.	Loss on ignition.	
I..	38·05	49·55	35·19	·28	·45	·31	1·13	13·70	= 100·61
	11·50								
II.	29·35	58·60	25·13	1·95	·50	1·49	1·70	10·90	= 100·27
	29·25								

From which may be calculated the formula—

$$\text{I. } 10{\cdot}78\ (Al_2O_3,\ 1.61\ SiO_3) + RO,$$
$$\text{II. } 2{\cdot}67\ (Al_2O_3,\ 2{\cdot}67\ SiO_3) + RO,$$

representing the following proportions:—

	I.	II.
Alumina to fluxes	10·78 : 1	2·67 : 1
Alumina to silica	1 : 1·61	1 : 2·67
Quotient	$\frac{10{\cdot}78}{1{\cdot}61} = 6{\cdot}70$	$\frac{2{\cdot}67}{2{\cdot}67} = 1$
Silica to fluxes	17·36 : 1	7·13 : 1

* Dingl. polyt. J., cc, 289—298.

This shows that although the proportion between silica and fluxes has decreased in a marked manner, the pyrometrical resistance has at the same time considerably decreased. The proportion of alumina present has sunk from 10·78 to 2·67, and the proportion of alumina to silica risen from 1·61 to 2·67. The quotient 1 shows therefore the inferiority of the second clay most strikingly, as compared with the quotient 10·78 of the first clay, and places the one in the seventh class—the last and lowest—the other in the second class of fire-clays.

From these and two more analyses* of Belgian clays from Namur, published by the author, which differed considerably in their pyrometrical value, but showed only slight analytical differences, and in which the less resistant qualities of fire-clay always exhibited a lesser proportion of silica compared with fluxes, the deduction to be drawn would be diametrically *opposed* to the one already referred to, had it not been, owing to the valuable pyrometrical determinations of E. Richters, that a definite measurable value has been arrived at, and the proportion between silica and fluxes appears consequently not only not essential and decisive for the value of different clays, but rather as a disturbing element, which stands in no relation at all to the proportion of alumina referred to. Viewed by itself, moreover, the proportions existing between silica and fluxes certainly furnish no criterion, since, as was shown by Richters in fire-clays, we have to deal with double compounds, and it is only by reviewing the proportions between alumina and fluxes, as well as between alumina and silica in their strict relationship to each other, that they acquire any practical value. The error lies in relying upon one or the other datum only. This the author proved by mixing silica and alumina in such proportions that an increase of alumina actually decreased the pyrometrical resistance of the mass. 100 parts of most finely powdered chemically pure quartz powder were intimately mixed with 1, 2, and 4 parts of alumina, and heated intensely in a furnace. The sample which contained 4 per cent. of alumina gave way sooner than that containing 2 or 1 per cent. Again, on mixing magnesia in like proportions with quartz, it was found that with the amount of flux the fusibility of the mixture likewise increases; but at the same time it is readily seen that the samples containing the alumina soften more and more readily than the corresponding samples containing the flux, and what must appear still more paradoxical, the alumina acts in this special case as a more powerful flux than the magnesia. Although such combinations of alumina and silica, in which the latter so largely prevails, are, properly speaking, called argillaceous sands, and do not occur as clays, the experiments show, nevertheless, that *all* the different

* Polyt. Journ., 1863, Bd., clxix, p. 413.

relations, and not merely *one*, should be taken into consideration. On further increasing the amount of alumina (2 per cent. at a time) and magnesia, it was again found that the alumina mixtures were more softened than the magnesia masses.*

The author holds that the extremely difficultly fusible silica (quartz powder), raises the infusibility of the respective mixtures in proportion as the chemical combination is less perfect, magnesia being evidently more slowly assimilated than alumina.

It is strongly insisted upon that the analysis of clays should be executed with the utmost rigour, since small discrepancies, even in the determination of the fluxes, impart to the formulæ a different character, whereby striking pyrometrical differences may be entirely effaced. By calculating formulæ from the duplicate analyses of one and the same clay, the one analysis furnished the formula, $5{\cdot}95(Al_2O_3,1{\cdot}38SiO_3)+RO$, or for every part of fluxes 5·95 of Al_2O_3, and for one part of alumina 1·38 of silica, *i.e.*, 8·21 of silica for every one part of fluxes: quotient = 4·31. The other analysis led to the formula, $6{\cdot}07(Al_2O_3, 1{\cdot}43SiO_3)+RO$, or for every one part of fluxes 6·07 of Al_2O_3, and for one part of alumina 1·43 of silica, *i.e.*, 8·68 of silica for every one part of fluxes: quotient = 4·24.

The possible difference is greatest in the case of the silica, less in the case of the alumina than in that of the fluxes—a result which is rather favorable to the alumina standard.

The author sums up as follows:—

To judge of the pyrometrical value of a fire clay, and to calculate the same from the chemical analysis, it is necessary to have regard:—

1. To the proportion of alumina and fluxes.
2. To the proportion of alumina and silica.

If in two or more samples of clays, sometimes the one, sometimes the other proportion prevails or recedes, a simple calculation, dividing the oxygen-quotient of alumina to fluxes by the oxygen quotient of alumina to silica (p. 964), expresses the pyrometrical value.

The quotient so obtained rises and falls with the increase or decrease of the fire-resisting qualities of a clay, and indicates unmistakeably the coincidence between pyrometrical and analytical results.

Exceptions to this law find their explanation in the respective characteristic physical conditions, the importance of which is thereby placed in the right light.

This quotient furnishes not only the measure, but forms also the proper criterion for the accuracy of the total observations made upon

* Observations made by repeatedly exposing the mixtures to very high temperatures, show that the same softening takes place *after* chemical combination has taken place, although the phenomenon is then less pronounced.

a fire-clay, and it enables us severally to control the analytical and pyrometrical results.

W. V.

Iodised Cotton. By C. Méhu.*

After reviewing briefly the means which were formerly in use, for the external application of iodine in cases of glandular swellings, goïtre, &c., the author proceeds to show, upon the evidence of considerable personal experience, that the more modern employment of aqueous, alcoholic, or ethereal solutions of iodine, in similar cases, is attended with many inconveniences. He proposes, therefore, to employ carded cotton, as a substitute for the above-mentioned solvents, this substance, when impregnated with iodine in a special manner, having proved in his hands equally efficacious as a remedy, and unattended with any serious disadvantages. The iodised cotton is prepared in the following manner. A quantity of perfectly dry cotton-wool, of good quality, is introduced into a stoppered flask of one litre capacity, together with about one tenth of its weight of finely powdered iodine, in such a manner as to distribute the iodine pretty evenly throughout the mass of cotton. The flask is then partially closed, and gradually heated in a sand-bath to expand the air. After a short time, it is firmly stoppered, and the heat raised, until the flask is filled with the vapour of iodine; this latter slowly combines with the cotton, causing it to assume a deep yellowish-brown colour. As soon as the whole of the iodine is fixed on the textile fibre, and the violet vapour is no longer visible, the operation is terminated, the whole process, if well conducted, being effected in about two hours. Twenty grams of cotton-wool will be found sufficient for one litre; it is also unadvisable to exceed the proportion of 10 per cent. iodine, since for general purposes, a cotton of half this strength is sufficiently active.

Although cotton can be made to absorb in this manner so large a proportion of iodine, it nevertheless still preserves in a great measure its original tenacity. Its colour is brown, and not black, which latter is sure to be the case if the source of heat employed be too high, or if its action be too greatly prolonged.

When exposed to the air, it loses its colour more or less entirely, becoming perfectly white if the percentage of iodine, and the temperature at which it was prepared were not too great; in fact, its remedial action depends upon the perfect but gentle manner in which it parts with its iodine: it possesses all the properties of this element, and

* Journ. de Pharm. [4], xiii, 388—391.

when applied to the skin, stains it yellow, producing a marked sensation of warmth, without causing the slightest irritation.

The author endeavoured to prepare iodised cotton, by steeping cotton-wool in concentrated solutions of iodine in ether and carbon disulphide, and then exposing the cotton to the air, to evaporate the solvent; it was found, however, that cotton prepared in this manner became very rapidly white, when allowed to remain even a short time in the air, and that generally, the employment of solutions to fix iodine on cotton, gave unsatisfactory results, since it necessitated the loss of large quantities of valuable liquid, out of all proportion to the quantity of iodine absorbed.

J. W.

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*Colouring of Butter with Carrot-pigment.**

THE colouring matter of carrots (carrotine), extracted by exhausting the dried and pulverised roots with bisulphide of carbon, is tasteless and scentless, and, consequently, better adapted to colouring butter than the generally used annatto.

C. H. G.

Albumin from Fish-roes. By W. GRÜNE.†

WHEN fish-roe can be obtained in large quantities, it may be made to yield a useful form of albumin. The fresh roe is to be rubbed on a fine metallic sieve with hard brushes, when much of the albumin will run through; the residue of cellular matter is then to be washed out with water containing $\frac{1}{300}$ of ammonia, and the whole liquid clarified by standing for some days. The clear portions drawn off are then evaporated in shallow vessels in a well ventilated space.

Fresh-water fish give an odourless product, but sea fish, especially if not quite fresh, yield an albumin which, when used for printing aniline colours, causes the cloth to develop an unbearable odour if it gets damp.

C. H. G.

Watering Streets with Saline Solutions.‡

IN Hamburg a road-space of 1,500 square metres was watered with 5,000 pounds of water holding in solution 250 lbs. chloride of calcium and 250 lbs. common salt. The surface was well wetted all over. A strong smell of ink was developed, the road did not remain moist for a

* Dingl. polyt. J., cc, 83. † Dingl. polyt. J., cc, 83.
‡ Dingl. polyt. J., cc, 85.

perceptibly longer time than when sprinkled with pure water, nor was the formation of a crust to be observed.

As the application of a sufficient quantity of salt to a large surface would be costly, and as it would require to be removed after every heavy rain, it does not appear that the process would be of much value, even if it fulfilled the purpose intended, of absorbing water enough from the air to keep the dust laid.

C. H. G.

French Silver Lacquer. (Dingl. polyt. J., cc, 83.)—Finely-divided tin precipitated from solution by zinc, and applied by admixture with varnish, &c.

Detection of Wood-pulp in Paper. By JULIUS WIESNER. (Dingl. polyt. J., cci, 156—159.)

Value of Canadian Oil as a Solvent for Extraction of Oil Seeds, compared with that of Bisulphide of Carbon. By H. POHL.*

THE same volume of the solvent is required in either case. 100 litres of Canadian oil weigh 68·0 kilos, while 100 litres of bisulphide of carbon weigh 126·5 kilos. 100 kilos of well purified Canadian oil cost 24 thlrs., and 100 kilos of bisulphide of carbon cost 20 thlrs.; therefore, it costs 9 thlrs. more for every 100 litres of solvent when bisulphide of carbon is used than in the other case.

C. H. G.

Composition of a French Dressing for Cotton Cloth. By C. FINCKH.†

ANALYSIS led to the following formulæ for its preparation: 4—5 parts palm oil are saponified by 2 parts caustic soda—dissolved up in more water—and mixed with 30 parts of glycerin of 30° Beck. 8 parts wheat starch are then stirred into the cooled mass, and the whole made up to 100 parts by water. For use, 6—8 lbs. of this mixture are to be boiled up with water and 100 lbs. of potato starch.

C. H. G.

Easy Determination of the Fat and Alkali in Soft (Potash) Soaps. By N. GRÄGER.‡

25—50 grammes of soap are dissolved in 150 c.c. water by aid of heat,

* Dingl. polyt. J., cci, 171. † Dingl. polyt. J., cci, 172.
‡ Dingl. polyt. J., cci, 174.

cooled, and mixed with an excess of salt, so that a soda-soap separates out; the latter is washed on a paper filter with a saturated solution of salt. In the filtrate the free alkali is estimated by normal acid. The precipitate is decomposed by warming with excess of normal acid, and the quantity of acid neutralised by the combined alkali determined by a standard soda solution. The cake of fat which separates in the last operation is dried and weighed, after adding to it, while melted, a known weight of stearin or paraffin to give it hardness.

C. H. G.

Notes on Ultramarin. By C. FÜRSTENAU. (Dingl. Polyt. J., cci, 176.)

Influence of Moist Ultramarin on Silver. By J. R. BRAUNSCHWEIGER.*

SILVER goods packed in paper, coloured by ultramarin, become tarnished owing to the evolution of sulphuretted hydrogen.

C. H. G.

Red, Green, and Blue Fire. By J. R. BRAUNSCHWEIGER.†

COLOURED fires, which may be burnt in dwelling rooms, and are not much influenced by damp, may be made thus:—

Red fire.—9 parts nitrate of strontia.
3 ,, shellac.
$1\frac{1}{2}$,, chlorate of potash.

Green fire.—9 parts nitrate of baryta.
3 ,, shellac.
$1\frac{1}{2}$,, chlorate of potash.

Blue fire.—8 parts ammonio-sulphate of copper.
6 ,, chlorate of potash.
1 ,, shellac.

The shellac is to be coarsely powdered.

C. H. G.

On Vulcanised Caoutchouc and the Tenacity of various sorts of Caoutchouc. By JAMES SYME, Sen. (Dingl. polyt. J., cci, 178, from the "Engineer," May, 1871.)

* Dingl. polyt. J., cci, 177. † Dingl. polyt. J., cci, 178.

Recipe for Dyeing Wool Amaranth-colour with Fuchsine. By C. L. PFUNDHELLER.*

FOR 20 lbs. cloth take $1\frac{3}{4}$ oz. ($3\frac{1}{2}$ loth) of diamond fuchsine; dissolve in 1 lb. glycerin by aid of heat, and filter; pour into a copper boiler containing hot water;† add 8 oz. (16 loth) of picric acid and 4 oz. crystallised soda. Boil fifteen minutes, and remove the scum which rises; put in the wetted cloth, work for thirty minutes, and boil. The cloth is now finished, and can be washed and dried, but the colour will be more lively if the washing is dispensed with.

C. H. G.

A Vegetable Cement of great Adhesive Power. By A. SELLE.‡

2 PARTS nitrate of lime, 25 water, and 20 parts powdered gum arabic rubbed together in a mortar form a transparent cement of remarkable strength, and applicable to wood, porcelain, glass, stone, &c. The surfaces to be united are painted with the cement, and bound together till drying is complete. C. H. G.

Glue for Paper Labels on Bottles.§

A MIXTURE of gelatin and dextrin boiled together in water. When the labels are dry, they should be covered with Dammar varnish.

Permanent Copying Paper for Printed Matter. By C. PUSCHER. (Dingl. polyt. J., cci, 183.)

Disinfection of Cesspools and Street Gutters. By Dr. ZIUREK. (Dingl. Polyt. J., cci, 184.)

S. Westphal's Process for Dyeing Black and Loading of Silk. (Dingl. polyt. J., cci, 179.)

Dyeing of Caoutchouc, Gutta-percha, &c., with Aniline Colours.‖

A. FORD has taken out a patent for colouring the above-named substances by immersing them in a warm aqueous solution of the aniline dyes. C. H. G.

* Dingl. polyt. J., cci, 179.
† The quantity of water is not mentioned.—C. H. G.
‡ Dingl. polyt. J., cci, 182. § Dingl. polyt. J., cci, 182.
‖ Dingl. polyt. J., cci, 180.

Use of Aniline Colours in Paper-making. (Dingl. polyt. J., cci, 180.)

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*Recovery of Stearic Acid from Oleic Acid.**

THE oleic acid pressed out of mixed fatty acids in the process of stearin-making retains much stearic acid, unless the weather is very cold. By cooling the oleic acid to 5° C., crystals of stearic acid separate out, and can be recovered by passing the mass into a centrifugal machine (like that used in sugar factories), the sieve of which is covered with a woollen cloth. The stearic acid retained in the machine is afterwards pressed.

C. H. G.

Technical Notes. (Chem. Centr., 1871, 496.)

Melting of Silver Residues.

To prevent loss of silver by absorption in the pores of the crucible, it is recommended to coat the interior of the latter with burnt borax and water.

Oxyhydrogen Light.

VAN MONCHOVEN advises the use of cylinders of burnt dolomite in place of ordinary lime, or simply marble, which becomes lime on use, and gives a regular light for several hours.

On Gold-ruby Glass. By W. MÜLLER. (Dingl. polyt. J., cci, 117—145.)

Coating of Metals with Nickel and Cobalt. By F. STOLBA. (*ibid.*, 145.)

Cleansing of Glass Vessels soiled with Petroleum. By F. STOLBA.†

THE cleansing material used is milk of lime, with which petroleum forms an emulsion.

* Dingl. polyt. J., cci, 181. † Ibid., 148.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

Apparatus for Estimating the Melting Points of Organic Bodies. By JULIUS LÖWE.*

THIS apparatus consists of, firstly, a cast-iron bath 17 × 11 × 7·5 centimetres in size, furnished with a cover of the same material, having a well 4·5 c.m. deep, and 2·5 c.m. wide, in its centre, and a small hole near one edge to afford escape for the vapours rising from the bath-liquid. The bath is filled with water or oil, and the well in the cover with mercury. Secondly, of a single battery cell, and an electro-magnetic alarum. A delicate thermometer is hung in the mercury, and covered by a glass tube, open at both ends, to prevent cooling. There also dips into the quicksilver a moderately thick, pointed platinum wire, the upper end of which is bent into a loop, and which, for convenience of fastening to a holder, is cemented into a bit of glass tube by sealing-wax. The loop of the platinum wire is connected with the zinc pole of the battery, and the mercury by another wire with the alarum apparatus, which is also connected directly with the other pole of the battery. The circuit being complete the bell rings. The platinum wire is withdrawn, cleaned by ignition, and its point is dipped two or three times into the melted substance under examination. On now replacing it in its former position, the current cannot pass owing to the layer of non-conducting substance covering the point of the wire. The temperature of the bath is raised till the current is re-established by the melting of the coating on the point of the wire, and the thermometer read at the first sound of the signal bell.

The test determinations quoted are highly satisfactory as regards uniformity.

For determining the point of solidification, the battery and alarum are rejected; a fragment of the material is melted on the surface of the mercury, and then allowed to cool slowly till it loses its transparency.

C. H. G.

* Dingl. polyt. J., cci, 250—254.

On Leidenfrost's Phenomenon. By R. COLLEY.*

THE author has endeavoured to determine the temperature of water, when in the spheroïdal state, by estimating the heating effect it produces when mixed with a given quantity of water contained in a suitable calorimeter, according to the method first employed by Baudrimont.† The calorimeter, a cylindrical vessel of thin polished silver, together with its contents, is carefully weighed before the experiment; the drop is then introduced, the rise in temperature is observed, and the weight again taken: the difference between these weighings gives the weight of the spheroïd. To avoid loss by evaporation during weighing, the calorimeter is kept covered by a silver plate. From the data thus obtained, the temperature of the spheroïd is calculated.

The spheroïds were produced in a dish of pure silver (weighing 173 grams), heated by a spirit lamp, or æolipile. The temperature of the dish is estimated by plunging it into a calorimeter and observing the rise in temperature produced.

The estimated temperature of the dish varied, in different experiments, from 237·3° to 779·7°; the weight of the spheroïd from 4·8236 grams to 23·6371 grams, and its estimated temperature from 90°·56 to 100°·34. A comparison of the experiments proves: 1st, that the temperature of water in the spheroïdal state is not constant, but is governed chiefly by two factors, the temperature of the dish, and the size of the spheroïd. The temperature of the spheroïd increases, therefore, although but slightly, with the temperature of the dish. The size of the spheroïd is, however, of greater influence. This, *a priori*, might have been supposed to be the case, since the temperature of the water will depend, on the one hand, on the amount of heat communicated by the dish, and, on the other, on the heat abstracted by evaporation; evaporation taking place on the surface only will naturally abstract proportionally less heat the larger the spheroïd.

These experiments further show that the opinion generally entertained, viz., that the temperature of liquids when in the spheroïdal state is always below their boiling point, is totally erroneous.

In none of the experiments could the author observe any formation of vapour in the interior of the spheroïd, evaporation being wholly confined to the surface.

Finally, the author endeavoured to measure the space between the lower surface of the spheroïd and the surface of the plate on which it rests. He estimates this distance (for small drops of 1 to 1·5 grm. weight) at 0·15 to 0·25 mm.

A. D.

* Pogg. Ann, cxliii, 125—141. † Ann. Chim. Phys. [2], lxi, 319.

On the Changes of Pressure and Volume produced by Chemical Combination. By M. BERTHELOT.*

A QUESTION has been raised whether at the moment when two gaseous bodies combine, with explosion, the pressure of the atmosphere ever predominates, so that the explosion acts inward and not outward. From considerations founded on the laws of Gay-Lussac and Mariotte, and also from experiment, Berthelot answers that this never takes place.

S. W.

Phenomena observed in the Distillation of certain Mixtures of Liquids Insoluble the one in the other. By IS. PIERRE and PUCHOT.†

THE authors in this communication give the results obtained by distilling water and amylic valerianate together. The following general conclusions are justified by experiment. That the temperature of ebullition remains constant, namely at 100°. The relative proportions of water and valerianate in the distillate were also constant. This relation is 65 to 35, *i.e.*, 13 volumes of water to 7 volumes of amylic valerianate.

S. W.

Thermal Effects of the Combination of Alcohols with Bases. By M. BERTHELOT.‡

THE thermal effects of the combination of bases with alcohols, phenols aldehydes, and with some compounds which, like salicylic acid, have a character intermediate between acids and alcohols, have been examined by the author with the object of throwing some light upon the chemical character of these bodies. He made use of calorimeters of platinum, holding from 600 cubic centimetres up to 1 litre and 2·25 litres of liquid; these were placed within a vessel of several concentric walls, partly lined with silver-plate, partly with tin-plate. The external compartment, being very large, was filled with water several days before the experiment. With the thermometers used, the temperature could be determined within $\frac{1}{200}$ of a degree. When the liquids operated upon contained half an equivalent, which was most frequently the case, they were called normal solutions, but sometimes they contained only one-quarter of an equivalent in 1 litre.

The thermal unit adopted was the heat necessary to raise 1 kilogram of water from 0° to 1°.

* Ann. Chim. Phys. [4], xxii, 134—139.
† Compt. rend., lxxiii, 441—443.
‡ Compt. rend., lxxiii, 663—681.

First Part.—True Alcohols.

I. *Ethyl Alcohol.*—It is well known that the alcoholates of barium, potassium, and sodium, are decomposed, gradually at least, by water; and that the presence of an excess of water does not permit their existence has been shown by the author by mixing a solution of alcohol (32 grams in 1 litre) with a solution of potassic hydrate (20·2 grams of K_2O in 1 litre). The rise of temperature observed was ·005°, which is so small that it falls within the errors of experiment, and may be neglected.

Also if the water be added after the mixing of the alcohol and the potassic hydrate ($160H_2O$ for C_2H_6O), the formation of the alcoholate is completely stopped, whilst with this degree of dilution the polyatomic alcohols still manifest their affinity for the alkalis.

II. *Glycerin.*—The thermal reaction taking place when the normal solutions are mixed is expressed as follows:—

$$(C_3H_8O_3 + Aq.) + (NaHO + Aq.) \text{ evolve } \cdot 372 \text{ heat-units.}$$

The dilution of the mixture obtained with five times its volume of water produces an absorption of ·363 heat-unit. The heat evolved on mixing being nearly equal to that absorbed on diluting, we may conclude that the compound formed in the first reaction is destroyed by the addition of so much water.

Further experiments showed that more heat was evolved on adding more glycerin, as well as on adding more sodium hydrate to a solution of glycerin containing 100 grams in 1 litre.

The author draws the following general conclusions:—

1. The reaction of glycerin upon the alkalis produces heat, not exceeding, in the case of the normal solutions, the $\frac{1}{40}$th part of the heat evolved by the combination of an acid with a base.

2. The heat increases with the number of equivalents of glycerin added to 1 equivalent of sodic hydrate, and *vice versâ*, without being proportional to the quantities added, either of the one or the other compound.

3. The heat diminishes as the dilution becomes greater, and none at all is evolved in the presence of 1200 H_2O. In short the compound formed in a concentrated solution is decomposed, with absorption of heat, on the addition of a sufficient quantity of water.

These phenomena, particularly the continual division of the base between the alcohol on the one side, and the water on the other, may be considered as characterising in general, and almost numerically, the combination of bases with alcohols; they differ from the phenomena attending the combination of bases with true acids, inasmuch as the neutral salts of the latter are formed in fixed proportions, and are not destroyed by the addition of any amount of water.

III. *Mannite.*—The thermic reaction observed on mixing the normal solutions was—

$$(C_6H_{14}O_6 + Aq.) + (NaHO + Aq. \text{ evolve } 1{\cdot}107 \text{ heat-units.}$$

The heat, although much more considerable than in the case of glycerin, is still only the $\frac{1}{12}$th part of the heat of combination of the true acids.

On adding the sodium hydrate successively, the following results were obtained:—

		Heat-units.
$(C_6H_{14}O_6 + Aq.) + \frac{1}{2}(NaHO + Aq.)$	evolve	+ ·696
$+ \frac{1}{2}(NaHO + Aq.)$	,,	+ ·372
That is ..... $+ (NaHO + Aq.)$	,,	+ 1·058

which value agrees with the first determination.

The addition of another $\frac{1}{2}(NaHO + Aq.)$	evolved	+ ·151
Total		+ 1·209

The evolution of heat does not, therefore, increase proportionately to the weight of sodium hydrate added.

The absorption of 1·430 heat-unit observed on diluting the solution obtained in this experiment, proved the decomposition of the compound formed in the concentrated liquid.

The reaction $(C_6H_{14}O_6 + Aq.) + (KHO + Aq.)$ produced 1·145 heat-unit that is, almost the same as when sodium hydrate is taken.

The action of calcic hydrate was examined by agitating it with a solution of mannite, made by diluting 1 litre of the normal solution with another litre of water, in order not to alter the proportions of the mannite and the water. Calcic hydrate being added, about $\frac{1}{3}$rd of an equivalent of this was dissolved, and the heat produced was found to be 1·467 heat-unit, allowance being made for the heat due to the solution of the calcic hydrate in water.

This number, not differing very much from those found for KHO and NaHO, renders it probable that the potassium and sodium compounds of mannite, when dissolved in the same quantity of water, have a constitution similar to that of the calcium compound, that is to say, that only one-third of the alkali remains in combination with the mannite, the other two-thirds being separated by the decomposing action of water.

In general, whether an alcohol combines with an acid to form an ether, or with a base to form an alcoholate, it appears that the amount of combination taking place always depends upon the quantity of

water present, which itself exhibits a strong tendency to combine with the acid or base.

Although in the reactions of etherification, equilibrium is attained after a considerable time only, whilst the formation and decomposition of the alcoholates in the presence of water seems to be instantaneous, it appears, notwithstanding this difference, that the combination of alcohols with acids, as well as with bases, obeys laws of chemical statics which, though less general and more simple, predominate in the formation of neutral salts.

IV. *Gum.*—300 cub. cent. of a solution of 1 part of gum in 100 parts of water, were mixed with 134 cub. cent. of a solution of sodium hydrate (24·5 per litre).

The heat evolved was	+ ·132 unit.
The addition of 137 cub. cent. of sod. hydr. produced	+ ·029 ,,
Finally, the addition of other 39 cub. cent. produced	+ ·006 ,,
	+ ·167

The heat absorbed on adding 5 volumes of water to the mixture was −0·174 unit, which, differing very little from the heat of combination, indicates an almost complete decomposition of the compound at first formed.

Second Part.—PHENOLS.

I. *Ordinary Phenol.*—100 parts of water dissolve 1 part and more of crystallised phenol, 2·075 heat-units being absorbed during the solution of every 94 grams (the equivalent) of phenol. When a solution of this strength acts upon an equivalent solution of sodium hydrate occupying a ten times smaller volume, the following reactions are observed:—

$(C_6H_6O + Aq.) +$	$(NaHO,Aq.)$	evolve	+ 7·34	heat-units.
$2(C_6H_6O + Aq.) +$	$(NaHO,Aq.)$	,,	+ 7·42	,,
$(C_6H_6O + Aq.) +$	$1\frac{1}{2}(NaHO,Aq.)$	,,	+ 7·46	,,
$(C_6H_6O + \frac{16}{18} Aq.) +$	$(NaHO,Aq.)$	,,	+ 7·39	,,

These numbers show, 1st, that only *one* phenate of sodium is formed; 2nd, that the evolution of heat is independent of the quantity of water present; and that, for these reasons, phenol, in accordance with other properties already known, seems to act towards the alkalis like one of the real acids, from which it differs by having only half as great a heat of combination.

It was found that—

$(C_6H_6O + Aq.) + (KHO,Aq.)$ evolve 7·51 heat-units.

when the potassium hydrate was added in successive portions, the heat increased proportionally to the weight of base added.

Another result—

$$(C_6H_6O + Aq.) + (NH_3 + Aq.) \text{ evolve } 2{\cdot}0 \text{ heat-units.}$$

Ammonium phenate can be decomposed by water, although only by a large quantity. The heat evolved on adding ammonia in successive quantities to phenol was not in proportion to the quantity added, as it was greater for the first portions than for the last. This behaviour of ammonium phenate is ascribed by the author to its being decomposed in the presence of water.

The hydrates of barium and calcium gave the following results:—

$(C_6H_6O + Aq.) + \frac{1}{2}(CaH_2O_2 + Aq.)$ evolved 7·30 and 7·53 heat-units.
$(C_6H_6O + Aq.) + \frac{1}{2}(BaH_2O_2 + Aq.)$,, 7·48 ,,

No more heat is produced by an excess of base.

The following reactions show how exactly the heat evolved was in proportion to the weight of base added:—

The 1st third of barium hydrate added evolved				2·50	heat-units.
,, 2nd	,,	,,	,,	2·53	,,
,, 3rd	,,	,,	,,	2·45	,,

It was also ascertained that the alkaline phenates yield their total heat of combination at the moment of their formation.

The fact that the amount of heat evolved by the combination of the hydrates of potassium, sodium, barium, and calcium, with phenol is very nearly the same, and that it is scarcely influenced by the greater or lesser quantity of water present, strengthens the conclusion arrived at before, as to the close relationship of phenol to the true acids.

II. *Picric Acid.*—That picric acid possesses the character of a real acid can be seen from the following results:—

The heat of combination with		potassium hydrate	was	13·8	units.
,,	,,	sodium	,,	13·7	,,
,,	,,	ammonium	,,	12·7	,,

The addition of a second equivalent of sodium hydrate produced no more heat. The behaviour of ammonia, on being added by successive thirds, is illustrated by the following table:—

The 1st third of an equivalent of ammonia added evolved				4·24
,, 2nd	,,	,,	,,	4·20
,, 3rd	,,	,,	,,	4·27
,, 4th	,,	,,	,,	0·00
				12·71

Therefore neither an acid nor a basic ammonium salt can have been formed.

The heat absorbed during the solution of picric acid was found = 7·00 units.

When potassium picrate was precipitated by mixing potassium nitrate (50 grams in 1 litre) with an equivalent volume of sodium picrate (52 grams in 1 litre), it was observed that—

$$(C_6H_2Na(NO_2)_3O + Aq.) + (NO_3K + Aq.) \text{ evolve } 10{\cdot}0 \text{ heat-units.}$$

The precipitation of picrate of ammonium by the analogous reaction gives + 8·70 heat-units for every equivalent of the ammonium picrate really thrown down.

It may be concluded that the introduction of the nitric residue into phenol is not a simple substitution, incapable of altering the chemical character of the generating body.

Third Part.—Aldehydes.

The solution of 1 equivalent of aldehyde in water produces 3·62 heat-units three-fourths of which are evolved almost instantaneously, whilst several minutes are required for the liberation of the remaining fourth. This large evolution of heat seems to indicate the formation of a definite compound, with a constitution perhaps resembling that of the hydrate of chloral.

On mixing equivalent solutions of aldehyde and of sodium hydrate, it was found that—

$$(C_2H_4O + Aq.) + NaHO + Aq.) \text{ evolve } 4{\cdot}326 \text{ heat-units.}$$

which is about one-third part of the heat of combination of the true acids.

Here, also, a little more than half of the heat is given off at once, whilst the second half requires four or five minutes. Dilution of the mixture obtained with five times its volume of water causes an absorption of 1·51 heat-unit, indicating a decomposition, at least partial, of the compound at first formed. It appears, therefore, that aldehyde partakes of the character of an acid as well as of a base; the combination with water, however, and the evolution of the heat of combination in successive unequal quantities, are phenomena peculiar to aldehyde.

Fourth Part.—Acids of a Mixed Character.

Salicylic, Lactic, and Tartaric Acid.—The first of these compounds behaves as a monobasic acid and as an acid alcohol at the same time. The heat evolved on mixing a solution of salicylic acid with one of

sodium hydrate was 14·6 heat-units, which number is in agreement with its first character. When a second equivalent of soda-solution was added, the liquid became too dilute to allow of the exhibition of any sensible increase of heat.

When crystallised salicylic acid was added to an equivalent quantity of normal solution of sodium hydrate, it was observed that—

$C_7H_6O_3$ (crystallised) + (NaHO + Aq.) evolve 5·27 heat-units.

When now a second equivalent of base was added, a further evolution of 2·00 heat-units took place, showing that indeed, in accordance with the second character of salicylic acid, a bibasic salicylate was formed, in the presence of 220 H_2O.

$$(C_7H_5NaO_3 + Aq.) + (NaHO + Aq.) = (C_7H_4Na_2O_3 + Aq.)$$

As, however, the addition of 5 times its volume of water to the liquid obtained by the above reaction caused the absorption of 2·05 heat-units, or nearly the same quantity of heat as that which had been liberated before, it appears that the compound formed is again decomposed.

We may, therefore, conclude that salicylic acid reacts upon the first equivalent of sodium hydrate in its character of a true acid, whilst it reacts upon the second in virtue of its alcoholic character.

In the case of lactic acid it was found that—

$(C_3H_6O_3 + Aq.) + \frac{1}{2}(NaHO) + Aq.)$	evolve	+ 6·81 heat-units.
$\frac{1}{2}(NaHO) + Aq.)$	,,	+ 6·52 ,,
Total		13·33

The addition of 1NaHO to the lactate already formed produced + ·21 cal., and the liquid thus obtained exhibited, on dilution with water, an absorption of ·7 heat-unit.

We perceive, therefore, that lactic acid possesses, to a certain degree, the nature of an alcohol, although the compound formed in virtue of this character is scarcely defined. Nearly the same remarks apply to tartaric acid.

Some observations were made on neutral sodium tartrate. On mixing its normal solution with an equivalent volume of normal sodium hydrate solution, it was observed that—

$(C_4H_4Na_2O_6 + Aq.) + (NaHO + Aq.)$ absorbed 0·5 heat-unit.

As the same solution of tartrate, on dilution with water, absorbed ·35 unit, it might be expected that the addition of sodium hydrate would, instead of absorbing any heat, produce about ·3 unit.

In short, the acids of a mixed character deport themselves as

acids, firstly, inasmuch as the quantities of heat evolved are proportional to the quantities of base added, as long as a neutral salt is being formed; and, secondly, inasmuch as the quantity of heat evolved is independent of the quantity of water present.

The alcoholic character, on the other hand, can be recognized in the reactions of bases which take place in concentrated solutions, but become rapidly enfeebled by dilution with water.

The character of these bodies of an intermediate nature can to a certain extent be traced in some mineral acids, for instance, in sulphydric acid, which, in the presence of water and of bases, behaves like a monobasic acid, the neutral salts of which may be represented by the formula HMS. Sodium hydrate acting upon a dilute solution of sodium sulph-hydrate, HNaS, does not produce any more heat than in acting upon a dilute solution of sodium salicylate; still in concentrated solutions a bibasic sodium sulphide can be obtained, as well as bibasic sodium salicylate. It appears, therefore, that sulphydric acid may be considered as an acid of a mixed character on the same ground as salicylic acid. R. S.

Thermo-chemical Researches in the Cyanogen Series. By M. BERTHELOT.*

THE object of Berthelot's researches, the results of which he has given in this paper, was to ascertain the amount of heat developed in the formation of the various compounds of cyanogen, and to compare this with the heats of combination of the elementary bodies. The experiments were conducted in a platinum calorimeter containing from 500 to 1,000 grams of water.

Hydrocyanic Acid.—The decomposition of a known weight of this body by hydrochloric acid was effected, and satisfied the equation:—

$$CHN + HCl + 2H_2O = CH_2O_2 + NH_4Cl.$$

The amount of heat generated was then observed. Diluting the products with a great quantity of water, the new disengagement was noted. A preliminary experiment gave the quantity of heat arising from mixing the same quantities of water and hydrochloric acid. Taking everything into account, the total quantity of heat was 10,900 units. From these data can be deduced the heat of formation of liquid and pure hydrocyanic acid from its elements, which will be − 37,700 heat-units.† If the acid is dissolved in a large quantity of water, + 400 units are disengaged. Deducting this, we obtain for the formation of dissolved hydrocyanic acid − 37,300 units. For the

* Compt. rend., lxxiii, 448—459.

† The unit of heat here adopted is the heat required to raise one gram of water from 0° to 1°.

formation of the gaseous acid, the heat of vaporisation must be taken into account, 5,700 units. This gives —43,400 heat-units for the gaseous body. The heat of combustion for the gaseous hydrocyanic acid will be therefore + 166,000 heat-units; for the liquid acid it will be + 172,000.

Hydrocyanic acid is therefore formed from its elements with absorption of heat, precisely like cyanogen, acetylene, sulphide of carbon, &c. Examining the other methods of forming this compound, the author shows that if it could be produced by directly combining cyanogen and hydrogen, each equivalent would absorb − 4,800 heat-units. This reaction, as shown by Gay-Lussac, and confirmed by himself, does not take place. Assuming the number from *à priori* considerations, we may compare it with the heat of formation of the analogous compounds of chlorine, bromine, and iodine.

ClH	+ 23900
BrH	+ 12300
IH.....	+ 800
CyH	− 2400

The first three are formed directly, but with increasing difficulty as they descend, the last not at all directly.

When free nitrogen and acetylene are acted upon by the electric spark, the union produces hydrocyanic acid with an absorption of heat equal to − 42,000 units.

The formation of hydrocyanic acid (formonitrile) from ammonium formate throws some light on the amides:—

$$CH_2O_2.NH_3 = CHN + 2H_2O.$$

This equation represents the full dehydration of ammonium formate. If it took place at ordinary temperatures with the solid salt, and with production of water and liquid hydrocyanic acid, there would be an absorption equal to − 13,400 heat-units; if the salt were dissolved, and the products were water and gaseous hydrocyanic acid, the absorption would be about −36,000 units. But the dehydration can be accomplished in two steps. First, formamide and water would be produced:—

$$CH_2O_2.NH_3 = CONH_3 + H_2O.$$

In the two phases of this dehydration equal quantities of heat should be absorbed. This, however, would be true for gaseous products only. The combination of the elements of water with the amide to form the ammonia salt disengages 1,400 heat-units; with the nitrile, 10,800. This is a new proof that disengagement of heat may result from simple hydration in the wet way, an important point in the study of the meta-

morphoses of the principal organic nitrogen-compounds, and in investigations on animal heat.

Potassium Cyanide.—Experiment gives the following data:—

Hydrocyanic acid in dissolving in forty times its weight of water emits heat equal to + 400 heat-units. Dilute hydrocyanic acid and dilute potash give + 2,960 units. Potassium cyanide, when dissolved in a large quantity of water, absorbs heat equal to — 2,960 units.

From these data the heat of formation of potassium cyanide from its elements may be deduced, namely, + 12,200 heat-units.

When cyanogen unites with potassium there is a disengagement of heat equivalent to + 53,000 units. This number is less than that which the analogous elements give in their union with potassium.

ClK.....	+ 102700
BrK	+ 89200
IK	+ 76300

Potassium cyanide when dissolved changes into potassium formate and ammonia, with disengagement of heat:—

$$CNK + 2H_2O = CHKO_2 + NH_3 \ldots + 8{,}500 \text{ heat-units.}$$

Ammonium Cyanide.—Ammonia in solution, and hydrocyanic acid also in solution, give on uniting about 1,300 heat-units. Recently prepared ammonium cyanide dissolved in 180 parts of water absorbs — 4,400 heat-units. From these data we can deduce the amount of heat disengaged when the two gases unite, namely 20,500 units. This is only half the amount which chlorine, bromine, and iodine give under similar conditions.

Mercuric Cyanide.—The formation of this cyanide from the elements themselves would be accompanied with an absorption of about — 41,000 heat-units.

The substitution of chlorine for cyanogen, with formation of mercuric chloride, disengages 25,000 heat-units; almost the same amount is disengaged when chlorine is substituted for cyanogen in hydrocyanic acid.

Potassium Cyanate.—This body, when decomposed by hydrochloric acid in presence of sufficient water to dissolve the liberated carbonic acid, disengages 28,800 heat-units. The solution of the cyanate in 300 parts of water absorbs — 5,200 heat-units.

From this we may deduce that in the formation of this salt from its elements 108,400 heat-units would be disengaged. The union of the cyanide with oxygen to form the cyanate would thus give 108,400 —12,200 = 96,200 units.

Potassium cyanate when dissolved changes by degrees into potassium carbonate and ammonium carbonate. In this decomposition

there is a disengagement of heat less by almost 6,500 units than the amount given in the reaction with hydrochloric acid. There is also a considerable disengagement of heat (13,000 units) when molten potassic cyanate is decomposed by steam.

Cyanogen Chloride.—From the heat set free in the decomposition of this body by potash, and the treatment of the mixture with hydrochloric acid, and from the determination of its heat of vaporisation, the heat of formation from its elements may be deduced.

In the liquid state.....	= − 14,500
In the gaseous state.....	= − 23,300

When cyanogen unites with chlorine

CyCl (liquid).....	= + 26,500
CyCl (gaseous).....	= + 17,700

Cyanogen Iodide and Bromide.—By similar considerations the heat of formation of these bodies from their elements may be arrived at. For the iodide it is found to be − 53,100, for the bromide − 40,000 heat-units.

These figures lead to the same general conclusions as those at which the author arrived in his experiments on the acetic compounds, as regards their chlorine, bromine, and iodine substitutions.

S. W.

Thermic Researches on the Electrolysis of the Alkaline Bases and the Sulphates of the Alkalies. By P. A. Favre.*

In a former communication the author has shown that the voltaic energy exerted by a Smee's battery may be represented as 15,000 heat-units. From this it would follow that the five elements, which he has hitherto used in his researches, would be represented by about 75,000 units, sufficient, it would seem, to electrolyse the sulphates of copper, hydrogen, cadmium, zinc, &c., as these bodies in fact require less than 75,000 heat-units (gram-degrees) for their decomposition. For the electrolysis, however, of the sulphates of the alkaline metals, it would appear, at first sight, that such a battery power would be incompetent. These considerations led him to operate in the following manner:—The electrolysis of the sulphates of the alkaline metals was accomplished by means of four cells of Bunsen's, and one cell of Smee's battery in a voltameter placed inside the calorimeter. The last-named element was only used to measure the amount of chemical action by the quantity of hydrogen liberated. The results of the decomposition of the oxides and sulphates of the alkalies were much below the amount which heats of combination seemed to demand. With the exception of their "ammonium oxide," the numbers obtained for the bodies ex-

* Compt. rend., lxiii, 768—780.

amined did not differ very widely. In examining the sulphates in a voltameter with a partition, the numbers obtained were about 14,000 heat-units below those obtained when there was no partition. This tends to show that when a partition is used, the base and acid do not reunite, with evolution of heat, during the electrolysis. Since it appeared from the above-mentioned experiments that the sulphates, and still more the oxides of the alkalies, did not require for their decomposition a force greater than was furnished by the original arrangement, the author returned to his former method. The following table gives the results arrived at for an equivalent of the body examined, 34,462 heat-units being deducted from the observed number, this being the thermic expression for the synthesis of water, the elements of which are set at liberty during the experiment:—

TABLE I.

Potassium oxide	16,528
Sodium ,, ...	16,418
Barium ,, ...	15,963
Strontium ,, ...	15,008
Hydrogen sulphate	14,012

The following gives the heat required for the electrolysis of an equivalent of each of the sulphates in solution:—

TABLE II.

Potassium sulphate	29,553
Sodium ,, ...	29,328
Ammonium ,, ...	27,538
Hydrogen ,, ...	14,012

These last numbers were obtained when the voltameter had no partition, but when a partition was used the numbers were much lower. Under these circumstances all the sulphates of the alkalies require the same amount of heat as that given for hydrogen sulphate in Table I.

With regard to "ammonium oxide," the following table gives the results:—

Ammonium oxide, concentrated solution	41,825
,, weak solution	42,041

The discrepancy between these numbers and those obtained from the other alkaline oxides, is due to the action of the liberated oxygen on the hydrogen still in composition. The following equations may throw some light on this. Under the influence of the current the "ammonium oxide" is decomposed, thus:—

$$(1) \qquad 3(NH_4)_2O = 3(NH_4)_2 + O_3.$$

The three equivalents of ammonium set at liberty decompose the water like potassium or sodium thus :—

$$(2) \qquad 3(NH_4)_2 + 3H_2O = 3(NH_4)_2O + 3H_2.$$

The oxygen (1) reacting on the ammonium oxide gives :—

$$(3) \qquad O + NH_4 = N + 2H_2O.$$

The first equation constitutes the electrolysis proper; the second represents a phenomenon which may be termed *synelectrolytic*, the heat being communicated to the circuit as would be the case with sodium or potassium under the same circumstances; in the third reaction the heat is not communicated to the circuit, and it may be termed meta-electrolytic.

The following conclusions seem to be justified by experiment:—The battery employed in the electrolysis of the alkalies and their salts succeeded in decomposing them only by virtue of its energy being strengthened by the oxidation of the metal itself. This oxidation is synelectrolytic, and the heat borrowed from the battery ought to be the same in the electrolysis of any of the salts of the alkalies. This appears to be the case from Table I. It seems probable also that, just as metals which decompose water when they are liberated by electrolysis develop variable quantities of heat which are, nevertheless, transmissible to the circuit, so likewise do metalloïd radicals which decompose water on their liberation, give variable quantities of heat, also transmissible to the circuit. This inference appears to be justified by the examination of sulphuric and nitric acids. It will result from this, that the quantity of heat borrowed from the battery for the decomposition of these bodies, cannot be considered as the thermic expression of their formation.

The author, in conclusion, gives some speculations as to the way in which the energy required to cause chemical decomposition can be transmitted by the circuit.

S. W.

On the Densities of Saline Solutions. By C. Alph. Valson.*

The author has experimented on the densities of solutions of various saline compounds; in each case an equivalent of the anhydrous salt in grams was dissolved in a litre of water. A salt may be represented by the formula MR, M being the metallic radical, and R the non-metallic. If now we pass from one solution of a salt MR, to another M'R, differing from the first only by the metallic radical, there will be

* Compt. rend., lxxiii, 441—433.

found a variation in the density peculiar to M′, which will be constant, and independent of the radical R. In the same way, by passing from MR to MR′, we have a variation peculiar to R′. Valson has named these variations "the moduli of the densities." The following table contains the moduli of the densities of various metallic and non-metallic radicals, taking as a starting point a normal solution of ammonium chloride, having the sp. gr. of 1·015, which is the least dense of all the salts examined. The number of salts which have been experimented on is 45, comprising 14 different metals, and 7 non-metallic radicals; the results all correspond to a temperature of 15°

Metallic radicals.	Equivalents.	Moduli of densities.
Ammonium (NH_4)	18	0
Potassium	39	30
Sodium	23	25
Calcium	20	26
Magnesium	12	20
Strontium	44	55
Barium	69	73
Manganese	28	37
Iron	28	37
Zinc	33	41
Copper	32	42
Cadmium	56	61
Lead	104	103
Silver	108	105
Non-metallic radicals.		
Chlorine	35·5	0
Bromine	80	34
Iodine	127	64
Sulphuric (SO_4)	48	20
Nitric (NO_3)	62	15
Carbonic (CO_3)	30	14
Bicarbonic (C_2O_5)	52	16

Suppose, for example, it is required to find the relative density of a normal solution of potassic nitrate; the number 1·015 is taken, and the moduli for potassium and the radical NO_3 are added, which gives 1·060, a number corresponding with the density of a normal solution as found by experiment. This rule is found not to be true for concentrated solutions, but it holds with dilute ones.

A. P.

On a new Thermo-electric Battery of Great Power. By A. VON WALTENHOFEN.*

THIS battery is the invention of Franz Noë of Vienna. The negative metal, an alloy similar to German silver, is drawn into wire; the positive alloy,† which is very brittle and somewhat less fusible than antimony, is cast into cylinders. The metals are joined together by casting the cylinder round the thickened end of the wire, in such a manner that the wire is in the prolongation of the axis of the cylinder. Over the wire a short copper cylinder is passed, and pushed up against the positive metal, but is prevented from coming in actual contact with it by the interposition of a piece of mica. Against these copper cylinders the flames of either gas or spirit lamps impinge, and are thereby prevented from fusing the positive alloy or burning through the wire. The elements are placed in double parallel series which, in the larger batteries, are so mounted that they may be used in various combinations, either for quantity or intensity.

The electromotive power (e) of one of these elements was found to be $e = 1{\cdot}24$ to $1{\cdot}36$ of Jacobi-Siemens' unit, while the author has found the electromotive power of a Daniell's cell equal to 12 of these units. It requires, therefore, 9 to 10 Noë's elements to equal 1 Daniell, whereas of Marcus's, 18 elements are necessary to obtain the same power. With larger batteries the electromotive power cannot, however, safely be raised above 1, otherwise superheating of parts is not to be avoided.

The larger battery examined consisted of 72 elements, which could be combined so as to form either, I, one series of 72 elements, or, II, one of 36 elements, or, III, 18 of four elements each. With each combination the electromotive power, per element, was found to be one of the above units; the resistance of a single element was 0·05. A Bunsen's element, charged with concentrated nitric acid and with sulphuric acid of 1 in 10, has an electromotive power of 20, and with a good porous cell a resistance of about 0·3 in elements of the usual size.

With a great external resistance, 20 of Noë's elements will thus be equal to 1 of Bunsen's.

With a small external resistance, 20 quadruple elements will be somewhat stronger than 1 Bunsen's. One Noë's element is about equal to 11 ordinary bismuth-antimony elements (temperature 0° and 100° C.). Even a single Noë's element produces considerable physiological effects when used with an induction apparatus.

The above-mentioned battery of 72 elements effects with combination I a copious decomposition of water; with combination II it sets in

* Pogg. Ann., cxliii, 113.

† The composition of these alloys is at present kept secret.

action middle-sized Ruhenthorff's coils; and with combination III, and spirals of thick wire, it produces powerful electro-magnets.*

In subsequent experiments it was found that the battery could safely be heated higher than was thought expedient in the former series; and it now gave a mean electromotive power of 1·14 per element, with a resistance of 0·054, a performance which will render a comparison with other batteries still more favourable to this new combination.

A. D.

Observations on Clean and Unclean Surfaces in Voltaic Action. By T. Bloxam.†

An unequal evolution of hydrogen-bubbles having been observed to take place from some portions of the platinum plate of a small battery, the subject was submitted to further enquiry.

In the first series of experiments, the time was observed which a pair of zinc and platinum plates requires to evolve 1 cubic inch of hydrogen. Commercial platinum was employed; the strip being 7 inches long by $\frac{1}{4}$ inch wide. Time, determined from a mean of many experiments, 22 minutes.

The strip cleaned by heating it in oil of vitriol: time, 14 minutes.

The strip passed through the fingers several times; time, 28 minutes.

The platinum again cleaned by igniting it in the flame of a Bunsen burner for one minute: time required, 15 minutes.

The strip cleaned by oil of vitriol, was dipped for a moment into a solution of common salt; the time now required for collecting a cubic inch of hydrogen was nearly doubled.

Copper negative plates in strips, similar to the platinum, were next employed. When cleaned with nitric acid and washed, they furnished 1 cubic inch of hydrogen in 21 minutes.

The strip passed through the fingers: time, $28\frac{1}{2}$ minutes.

A plate of copper, oxidised by heating it in air, furnished the hydrogen in 10 minutes.

The last experiment suggested the trial of platinised silver, which, arranged in the same manner as in the foregoing experiments, gave 1 cubic inch of hydrogen in $2\frac{1}{4}$ minutes. A strip cleaned with oil of vitriol as usual: time $2\frac{1}{4}$ minutes. A strip soiled by the fingers: time, 3 minutes.

To ascertain the amount of *resistance* offered by platinum plates, under similar circumstances, a cell of Smee's battery was examined by the galvanometer; all other conditions remaining the same. The negative plate not chemically clean: deflection = 52°.

* The battery may be obtained from M. Noë, Tünfhaus, Tellgasse, No. 12, Vienna, for about £4.

† Chem. News, xxiv, 123.

Negative plate chemically cleaned, 57°. Negative plate soiled by the fingers, 48°. The platinum removed from the surface, gave deflection = 50°.

A final experiment was directed to ascertain the influence of chemically clean surfaces upon electrolysis. The mixed gases were evolved from the electrodes of a two-cell Bunsen battery; one cubic inch was collected in 2 minutes. When the electrodes were cleaned with hot oil of vitriol, and the battery freshly started, it required $1\frac{1}{4}$ minutes only to furnish the same quantity of gas.

J. W.

On the Spectra of Simple Gases. By A. J. Ångström.*

The author has experimented on the spectra of several gases at varying pressures. One of Geissler's tubes, filled with atmospheric air, was gradually exhausted by a mercurial pump, the spectra being obtained by using an induction coil. Ångström states that he observed successively the following spectra:—1st, the ordinary spectrum of air; 2nd, the band spectrum of nitrogen (Plücker's spectrum of first order); 3rd, that of carbonic oxide; and, 4th, when the rarefaction had reached its maximum, the lines of sodium and chlorine. Added to this may be the spectra of mercury (from the mercurial pump), and of sulphur from the sulphuric acid used in drying the gas. This is given as an instance of the variety of spectra which might be attributed to a single gas.

Plücker found that he could obtain from rarefied hydrogen a second spectrum, differing from the ordinary spectrum of that gas, which contains 3 lines, by containing a number of lines extending from C to beyond D; this spectrum generally presents itself at the same time as the ordinary well known three lines. On placing a tube of this kind in front of a revolving mirror, two distinct images are reflected, one being an isolated line of short duration, and the second lasting much longer. The latter image disappears immediately on making the discharge from the coil disruptive. This Ångström believes will account for the two spectra observed by Plücker. Ångström has made experiments with this spectrum, and concludes from them that it agrees with the spectrum of acetylene. Wüllner, however, has described a third spectrum belonging to hydrogen, which, from a comparison of Wüllner's measurements with those of the spectrum of sulphur, Ångström believes to be identical with the spectrum of the latter body.

Ångström therefore persists in his opinion that hydrogen has only one spectrum, the same that is observed in the spectrum of the sun and stars.

* Compt. rend., lxxiii, 369—375.

Wüllner also found that three spectra could be obtained from oxygen under varying pressures.

Ångström has compared the readings of spectrum No. 2 with those obtained from carbonic oxide, and shows that they agree closely. Some of the readings of oxygen spectrum No. 3 are compared with the measurements of the chlorine spectrum, which agree so well that Ångström believes that this spectrum is no other than that of chlorine. In no case, however, does the actual experimental comparison of the spectra, as obtained by Wüllner, seem to have been made with the spectra of the substances with which Ångström asserts them to be identical.

Magnetism has a peculiar effect on the various spectra. Thus a tube filled with hydrogen dried over sulphuric acid, which gives Plücker's spectrum No. 2, exhibits, under the influence of magnetism, the lines of sulphur, or as Wüllner regards them, the hydrogen spectrum No. 3, whilst the spectrum of carbonic oxide appears round the electrodes. In certain cases magnetism appears to act in the same way as the addition of a condenser to a Ruhmkorff coil, although it also appears to have a sort of chemical action in inducing the production of certain combinations which gave different spectra.

A. P.

Observations on the Colour of Fluorescent Solutions. By HENRY MORTON.*

THE author having observed that a particular specimen of asphalt, yielding a yellow solution with alcohol, and an orange solution with turpentine, presented in the former case a blue, and in the latter a green fluorescence, was led to infer that the green colour was due, not to the development of green rays, but to the absorptive action of the coloured solution; and, prosecuting the enquiry, he has decided that all fluorescent bodies, such as solutions of chlorophyll, uranium nitrate, quinine, &c., emit light of the same colour by fluorescence, viz., blue, the colour, however, being in all cases not of a single tint or refrangibility, but yielding a continuous spectrum, in which the more refrangible rays predominate.

When the green fluorescence above mentioned was examined with the spectroscope, no increase could be observed in the green or yellow portions of the spectrum, and when, by filtration through charcoal, the solution was much reduced in colour, the green tint of the fluorescence disappeared in a corresponding degree.

In the same manner the fluorescence of tincture of turmeric, which in the concentrated state appears deep red, was found to change to

* Chem. News, xxiv, 77.

green when the liquid was diluted until its colour was reduced to yellow, and by continuing the dilution, or by decoloration, until the liquid was of a very light tint, the fluorescence became distinctly blue. Similar phenomena were observed when chlorophyll was substituted for the turmeric.

Respecting uranium nitrate, which in the solid state gives a brilliant green fluorescence, and the spectrum of which undoubtedly abounds in green rays, it was found in solution to give a very feeble fluorescence, far inferior to that of turmeric, and not having a greener tint than would be due to its yellow colour. From these results the author concludes that the molecules of fluorescent bodies in solution do not appear to be capable of restricting their vibrations to limited rates, but move at rates corresponding to all refrangibilities, having simply an excess of the higher ones.

It must be admitted, however, that the same substances in the solid state may act in a different manner, since a blue fluorescence cannot be observed with uranium nitrate, nor yet with certain solid hydrocarbons.

J. W.

The Dichroism of the Vapour of Iodine. By T. ANDREWS.*

THE fine purple colour of the vapour of iodine arises from its transmitting freely the red and blue rays of the spectrum, while it absorbs nearly the whole of the green rays. The transmitted light passes freely through a red copper or a blue cobalt glass. But if the iodine vapour be sufficiently dense, the whole of the red rays are absorbed, and the transmitted rays are of a pure blue colour. They are now freely transmitted as before by the cobalt glass, but will not pass through the red glass.

A solution of iodine in carbon bisulphide exhibits a similar dichroism, and, according to its density, appears either purple or blue when white light is transmitted through it. The alcoholic solution, on the contrary, does not exhibit any dichroism.

J. W.

The Action of Heat on Bromine. By T. ANDREWS.†

IF a fine tube is filled one-half with liquid bromine, and one-half with the vapour of bromine, and after being hermetically sealed is gradually heated till the temperature is above the critical point, the whole of the bromine becomes quite opaque, and the tube has the aspect of being filled with a dark red and opaque resin. A measure of the change of

* Chem. News, xxiv, 75. † Chem. News, xxiv, 75.

power of transmitting light in this case may be obtained by varying the proportion of liquid and vapour in the tube. Even liquid bromine transmits much less light when heated strongly in an hermetically sealed tube than in its ordinary state.

J. W.

Inorganic Chemistry.

Experiments on the Electrisation of Air and Oxygen for the Production of Ozone. By AUGUSTE HOUZEAU.

IN working an electric machine, ozone is invariably produced, but when this body is required in large quantities for experimental purposes, its production is always beset with difficulties. To account for this, and to ascertain the exact circumstances required for the generation of ozone, the author investigated the subject anew.

When a tube in the form of the letter Y has its lower limb inserted into the neck of a flask which acts as an aspirator, and two wires forming the electrodes of an induction-coil are passed down the branch tubes so as nearly to meet at the juncture of the three limbs, no ozone is produced when the *brilliant* spark passes. But if the two upper limbs are brought into contact through their whole length, and the wires are separated to such a distance as will not permit the *brilliant* spark to pass, the production of nitrous bodies which took place in the former arrangement instantly ceases, and ozone is generated in quantity. Under these circumstances the brilliant spark has given place to a soft violet light, visible only in darkness, and extending along the electrodes. These conditions were ascertained to be the most favourable for the production of ozone.

The apparatus employed by the author in his investigations was of the following form:—Through a cork inserted into the opening of a glass foot-cylinder, passed a tube reaching almost to the bottom, and another bent at right angles was connected with a Will's bulb-tube containing dilute sulphuric acid and neutral potassium iodide, for the estimation of the ozone produced. Through the same cork a thick platinum wire was passed (insulated by glass from the cork), parallel to the side of the vessel and near it. This the author calls the interior electrode. Another platinum wire was fixed with silk to the exterior of the vessel, parallel to the interior wire; this is termed the exterior electrode. When the two wires are connected with the poles of an induction coil in work, the characteristic odour of ozone is immediately perceived.

Making use of this apparatus, Houzeau arrived at the following

facts:—Acting on confined air he found that the production of ozone was greater at the negative than at the positive electrode, and that it decreased in quantity the further the electrodes were separated. When the air was renewed constantly, and the quantity generated at one only of the electrodes was estimated, it was again found that ozone was produced in greater quantity at the negative than at the positive pole. The greater the length or surface of the wires, the greater was the quantity produced. When the two electrodes were used, other things being equal, the quantity was also greater. Modifying his apparatus so that the two electrodes could be surrounded by thin glass tubes, either opened or closed (*électrodes fourrées fermées ou électrodes fourrées ouvertes*), he found that ozone was also produced when the electrodes were enclosed, so as to prevent contact with the exterior air, but a much larger quantity was generated when a current of air was allowed to pass through the tubes, and this varied as the velocity of the current of air. It also varied with the intensity of the electric current, and the lower the temperature of the air the greater was the production of ozone.

Acting upon oxygen, he found that, volume for volume, more ozone was produced from oxygen than from air. When pure oxygen was used, the product was necessarily free from nitrogen compounds, which always accompany it in small quantities when air is used.

Guided by these experiments, the author has constructed an apparatus for the generation of this body, the particulars of which he promises to give in a future communication.

S. W.

On the Preparation and Properties of a Sulphide of Selenium. By A. Ditte.*

When a concentrated solution of selenious acid is treated with sulphuretted hydrogen, a precipitate is obtained which is plastic and does not appear homogeneous; but if care be taken to use a very dilute solution and to maintain the temperature between 0° and 5°,—and if the sulphuretted hydrogen be first passed through a wash-bottle filled with fragments of ice,—the precipitate which forms is in a state of fine powder, of a lemon-yellow colour, and collects easily at the bottom of the vessel, leaving a colourless liquid above. This precipitate well washed and dried in vacuo, treated with enough carbonic sulphide to moisten it, and left to itself for some days, is transformed into crystalline scales, while the carbonic sulphide is saturated with dissolved sulphur. More carbonic sulphide is added, removed after a few moments, and the product is washed with pure benzol, which

* Compt. rend., lxxiii, 625.

removes the rest of the free sulphur, washed again with alcohol, and dried in a vacuum.

So obtained, the compound exhibits the form of small orange-yellow, brilliant and transparent scales, corresponding in composition to the formula SeS. The mean of four closely agreeing experiments gave S = 28·68 per cent., and Se 71·40 per cent; calculation for SSe gives S = 28·72 and Se = 71·28.

The density of the compound at zero = 3·056; at 52°, it is 3·035; its specific heat is 0·1274. Under the influence of heat, it melts and decomposes, giving off mixed vapours of sulphur and selenium.

It is insoluble in water and in ether, is slowly decomposed by absolute alcohol, which causes its constituents simply to separate. It dissolves in excess of carbonic sulphide, but cannot be recovered by evaporation, for the solution first deposits almost pure sulphur, and afterwards crystals containing more and more selenium, till at last selenium containing very little sulphur is obtained.

C. H. G.

Second Note on the Preparation and Properties of a Sulphide of Selenium. By A. Ditte.*

When sulphuretted hydrogen is passed into neutral potassic selenite with the precautions indicated in the former note, the precipitate takes the form of a red-brown powder, in which yellow points of sulphur can be readily distinguished. This precipitate, when treated as before with carbonic sulphide, crystallises much more quickly than that formed in acid solutions, but the crystals are of a dark red-brown colour, owing to the alkaline sulphide having abstracted a minute portion of the sulphur, and are more easily decomposed by alcohol.

The density of the compound at zero is not equal to the mean density of its elements. This mean density is comprised between the two numbers $\Delta_1 = 3{\cdot}2067$ (prismatic sulphur and amorphous selenium) and $\Delta_2 = 3{\cdot}4866$ (octahedral sulphur and crystallised selenium), while the density found for the sulphide is $D = 3{\cdot}0566$; therefore the combination of the elements is accompanied by expansion. The compound occupies a volume superior to the volume of its elements, and its negative contraction is comprised between the two values—

$$C_1 = 1 - \frac{\Delta_1}{D} = -\ 0{\cdot}0493, \text{ and } C_2 = 1 - \frac{\Delta_2}{D} = -\ 0{\cdot}1409.$$

The heat of contraction, per equivalent, calculated by the aid of these numbers, lies between − 6050 and − 2150 units of heat. When oxidised with hypochlorous acid, the sulphide of selenium disengages

* Compt. rend., lxxiii, 660.

for each equivalent, about 10500 units of heat *more* than a mixture of insoluble sulphur and metallic selenium, and 5500 units more than a mixture of prismatic sulphur and vitreous selenium; consequently, it belongs to the class of explosive bodies.

C. H. G.

On the Apparent Volatilisation of Silicon and Boron. By L. Troost and P. Hautefeuille.*

In experiments made on the oxidation of silicon at the expense of carbonic oxide, the presence of fibrous tufts of silicic anhydride, sometimes mixed with fused silicon, at some distance from that portion of the tube occupied by the fused mass, led the authors to determine under what conditions silicon, a body perfectly fixed, can give rise to a body equally fixed at some distance from the generating body. It was found that traces of silicic chloride or fluoride were necessary to produce this effect. Silicon was fused in a porcelain tube in a current of hydrogen, and then a little fluoride allowed to pass along with the gas. As the fluoride passed over the melted silicon, it produced a thick cloud, which settled as a reddish powder further up the tube. If a very slow current of silicic fluoride is passed along in this way, a thin cloud only is produced, which is deposited as a ring at the part of the tube not sufficiently heated to appear luminous. The ring thus produced consists of a network of crystals of silicon, some of which are measurable, and very brilliant; the powder produced by the rapid current of gas is amorphous silicon. The electric arc and also the induction spark passing between two carbon points, decompose silicic fluoride, producing amorphous silicon. If two points of fused silicon are used instead of the carbons with the induction spark, a volatile white body is seen to be formed; this is found to be a subfluoride of silicon.

Silicic chloride can be used in a similar manner to produce this apparent volatilisation of silicon. In one experiment 5 grams of silicon were carried from one part of the tube to another in less than an hour. A very small quantity of the chloride is sufficient to volatilise a large quantity of silicon; the temperature at which the deposits take place seems to be from about 500° to 800°.

In that part of the tube which contains the fused silicon and is most strongly heated, the chloride or fluoride must take up an excess of silicon, which is again deposited on the cooler parts of the tube. The compounds thus produced possess therefore the singular property of being formed at a temperature higher than that at which they decompose. The two new bodies are very stable at a white heat, and at

* Compt. rend., lxxiii, 443–447.

ordinary temperatures, but dissociation takes place at a red heat with the fluoride, and at about 700° with the chloride. The subfluoride can with difficulty be isolated by very rapidly cooling it from its original high temperature; the subchloride is, however, more easily obtained: for on passing a rapid stream of silicic chloride over fused silicon, so that it produces amorphous silicon, the greater part of the subchloride escapes decomposition.

A. P.

Note on a Subchloride of Silicon; occasioned by the preceding Communication. By C. FRIEDEL.*

THE author recounts some unfinished experiments on the ethylic series of silicon. The tri-iodide of silicon Si_2I_6, obtained by reduction of the tetraiodide by pulverulent silver, breaks up on distillation into tetraiodide and a fixed subiodide. When silicon tri-iodide is heated with mercury dichloride, a brisk reaction takes place, and there distils over, besides silicon tetrachloride, another chloride much less volatile, which dissolves in potash with disengagement of hydrogen. By the action of water on silicon tri-iodide, a compound $Si_2O_4H_2$ is produced, which dissolves in potash, with disengagement of hydrogen and formation of potassium silicate. By analogy then, the above-mentioned chloride is regarded as the trichloride Si_2Cl_6.

Some experiments made by Friedel and Ladenburg confirm the observations of Troost and Hautefeuille (p. 999); on passing silicon tetrachloride for several hours over crystallised silicon heated in a porcelain tube to a temperature a little below the melting point of the latter substance, acicular crystals of silicon were found deposited in the colder parts of the tube; doubtless the result of successive combination and decomposition.

W. H. D.

On the Subchlorides and Oxychlorides of Silicon. By L. TROOST and P. HAUTEFEUILLE.†

WHEN tetrachloride of silicon is passed over fused silicon contained in a porcelain tube, which is heated nearly to the softening point of porcelain, a liquid is obtained, consisting of the tetrachloride, together with a small quantity of the subchlorides of silicon. The tetrachloride was passed backwards and forwards five or six times over the silicon; in order to prevent, as far as possible, decomposition of the subchlorides, a central cooling tube was employed, as in Deville's experiments

* Comptes rend., lxxiii, 497 † Comptes rend., lxxiii, 563.

on dissociation, through which water at 60° was passed. Air was carefully excluded from the apparatus, to guard against formation of oxychlorides.

The separation of the tetrachloride of silicon, boiling at 59°, from the liquid product of these operations, is very easy; this is not the case with the other chlorides, repeated fractional distillation being required, or employment of appropriate reagents. The authors succeeded finally in obtaining a protochloride and a trichloride of silicon.*

Properties of the Trichloride of Silicon.—This body is a colourless and very mobile liquid, having a specific gravity of 1·58 at 0°. At − 14° it solidifies, forming large crystalline plates. It boils at 146°—148°; the density of its vapour, taken at 239·4°, is 9·7, corresponding to the formula Si_2Cl_6, the correctness of which was, moreover, confirmed by analysis.

The vapour of the strongly heated trichloride takes fire spontaneously in the air; heated in closed vessels, the trichloride begins to decompose very slowly at 350° (into tetrachloride and silicon); by heating for 24 hours to 440°, about nine-tenths of the chloride employed is decomposed; at 800° the decomposition is complete.

The trichloride of silicon is attacked by cold aqueous solution of ammonia, silica and hydrogen being produced. In contact with pure water at zero, it gives a hydrate of the tri-ioxide identical with that obtained by Friedel and Ladenburg from the tri-iodide. Some new properties of this sesquioxide are given; in the cold it reduces potassium permanganate very rapidly, and chromic acid very slowly; it has no action, at the ordinary temperature, on solutions of chloride of gold or selenious acid.

Dichloride of silicon is a liquid which was found mixed with the trichloride, especially when the formation of the latter body is accompanied by that of highly condensed oxychlorides of silicon. Its vapour-density and boiling point have not yet been determined, as it retains pertinaciously small quantities of oxychlorides. Decomposed by ammonia-water, it evolves a larger proportion of hydrogen than the trichloride. By contact with water at zero, it gives rise to a hydrated oxide, which reduces, not only potassium permanganate and chromic acid, but also solutions of chloride of gold and selenious acid, with separation of metallic gold and red selenium respectively.

Subfluoride of silicon is a white, very light powder, produced by passing the tetrafluoride over silicon heated nearly to the softening-point of porcelain. It is probably a trifluoride, as in contact with

* Troost and Hautefeuille employ the term sesquichloride, as the number they use for the atomic weight of silicon is the half of that generally adopted.

water it yields an oxide which gives the same characteristic reactions as the oxide from the trichloride.

Production and Preparation of the Oxychlorides of Silicon.—In the course of their experiments on the action of tetrachloride of silicon on silicon, the authors constantly met with the oxychloride Si_2OCl_6, obtained by Friedel and Ladenburg, and also with other oxychlorides, which were less volatile, and had a higher equivalent. The best method of preparing these latter compounds was found to lie in the direct action of oxygen on the oxychloride Si_2OCl_6. A mixture of oxygen and vapour of the oxychloride was passed several times backwards and forwards through a glass tube filled with fragments of porcelain, and heated by a gas-furnace. At the end of the operation, a liquid was obtained, containing, besides the excess of the oxychloride employed, a whole series of oxychlorides of silicon. They were separated, their percentage composition determined, and their condensation in the state of vapour at 440° was also determined; the study of their chemical properties is reserved for a future occasion. The following have been obtained:—

Formula.	Boiling point.	Vapour density actually found (at 440°).
Si_2OCl_6, corresponding to 2 vols.....	136°—139°	(F. and L.)
$Si_4O_4Cl_8$,, ,, ...	198°—202°	15·5
$Si_8O_{10}Cl_{12}$,, ,, ...	About 300°	31·2
$Si_2O_3Cl_2$, empirical.....	Above 400°	—
$Si_4O_7Cl_2$,, ...	Solid at 440°	—
$Si_4O_3Cl_{10}$, corresponding to 4 vols...	152°—154°	Said to agree sufficiently with the calculated number.

Finally, an oxychloride of zirconium has been obtained, corresponding to the most abundantly produced oxychloride of silicon Si_2OCl, and a titanium derivative, the percentage composition of which is expressed by the formula $Ti_2O_3Cl_2$.

W. H. D.

On Natural Nitrification. By M. Berthelot.*

The fullest experiments that have been made on the chemical conditions of nitrification are even now those of MM. Thouvenel† although they were made nearly a century ago. These experiments show that nitrification is principally effected upon the gaseous products of putre-

* Ann. Chim. Phys. [4], xxii, 87—96.

† Mem. de l'Acad. des Sciences (Sav. étrang.), xi, 1787.

faction; that it proceeds better in the presence of alkaline or earthy salts than in their absence; and that it scarcely takes place but with carbonates, and not at all with sulphates.

The results of these experiments are to be accounted for by considering that the disengagement of the ammonia furnished by the nitrogenous organic matters occurs only in an alkaline medium; that it cannot take place in one capable of forming by double decomposition only fixed and neutral salts such as the sulphate; and that, on the other hand, its occurrence is facilitated when the liquor can give rise to a volatile ammoniacal salt, like the carbonate. The presence of a fixed alkali or of an alkali carbonate determines also the generation of ammonia at the expense of the nitrogenous matters. Moreover, the presence of an alkali or of a salt with alkaline reaction is very efficacious in accelerating the oxidation of organic matters by the air at ordinary temperatures.

Even the way in which the oxidation of the ammonia proceeds, aids in explaining the efficacy of the fixed alkalis and their carbonates. For the slow oxidation of ammonia develops nitric acid, and this can only unite with the unchanged ammonia to form ammonia nitrate, a fixed salt without alkaline reaction. But the presence of an alkali carbonate preserves the alkalinity of the liquor, as it transforms the ammonia nitrate into fixed alkali nitrate and into ammonia ready for an ulterior oxidation.

A comparison of these different circumstances with the quantities of heat disengaged by them, throws considerable light upon the degree of their participation and importance in nitrification.

Transformation of ammonia into nitric acid and into ammonium nitrate:

Ammonia ..... $NH_3 + O_4 = NO_3H + HO_2$
Ammonia nitrate .... $2NH_3 + O_4 = NO_3H.NH_3 + H_2O$.

The formation of gaseous ammonia from its elements, $N + H_3 = NH_3$, disengages, according to Favre and Silbermann, 22700 heat-units (22500); that of dissolved ammonia, $N + H_3 + n\text{Aq.} = NH_3 + n\text{Aq.}$, disengages 31,500; lastly, the formation of water, $H_2 + O = H_2O$, disengages 69,000 or 59,000, according as the water is produced in the liquid or in the gaseous state.

Hence it follows that the oxidation of ammonia disengages the following quantities of heat, according to the nature and the state of the products to which they give rise:—

(1) *Formation of nitrogen:*

$$2NH_3 + 3O = N_2 + 3H_2O.$$

Ammonia gaseous and water gaseous..	177000−45000=132000
Ammonia dissolved and water liquid..	207000−63000=144000
Ammonia gaseous and water liquid ..	207000−45000=162000

(2) *Formation of nitric oxide:**

$$2NH_3 + 5O = N_2O_2 + 3H_3O.$$

Ammonia gaseous and water gaseous	146000
Ammonia gaseous and water liquid	176000

(3) *Formation of nitrous acid:*

$$2NH_2 + 6O = 2NO_2H + 2H_2O.$$

Ammonia gaseous, water liquid, nitrous acid dilute	163000

(4) *Formation of nitric acid:*

$$2NH_3 + 8O = 2NO_3H + 2H_2O.$$

Ammonia gaseous, water and nitric acid gaseous, about.....	162000
Ammonia gaseous, water liquid, nitric acid dilute..	217000
Ammonia dissolved, nitric acid dilute.....	199000

(5) *Formation of ammonia nitrite in solution:*

$$2NH_3 + 3O = NO_2H.NH_3 + H_2O.$$

Ammonia gaseous, nitrite dissolved, about.....	104000

The reaction of the same bodies producing water and nitrogen develops half as much more heat (162000); ammonia nitrite also very readily decomposes into nitrogen and water.

(6) *Formation of ammonia nitrate in solution:*

$$2NH_3 + 4O = NO_3H.NH_3 + H_2O.$$

Ammonia gaseous, nitrate dissolved.....	131000

(7.) Transformation of ammonia nitrite in solution into nitrate:—

This transformation, and that of any other dissolved nitrite into a nitrate of the same base, which several authors believe occurs in nitrification, disengages about 27000 units of heat.

These figures show that the formation of the oxygenated compounds of nitrogen by the oxidation of ammonia is always accompanied by a disengagement of heat; it can, therefore, always take place without the assistance of any external energy, a circumstance which, in the case of certain of the oxides of nitrogen, happens only when they are formed by using free nitrogen. Hence these oxides are much more easily obtained by setting out with ammonia.

* Ann. Chim. Phys. [4], xxii, 75.

Reciprocally—but this is foreign to the question of nitrification—the formation of ammonia by the reaction of hydrogen with the different oxides of nitrogen, always disengages more heat than the same formation effected by means of free nitrogen, a fact which explains the much greater facility of the former reaction.

Various experiments to see if free ammonia could be oxidized directly by the air at ordinary temperatures, with the aid of time, have all proved unsuccessful. In spite of these negative trials, the oxidation of ammonia during nitrification cannot, apparently, be called in question, but the conditions which preside over it are still only imperfectly known.

Integral transformation of ammonia into potassium nitrate:—

The ammonia having oxidized into ammonia nitrate, this salt becomes transformed by the potassium carbonate into potassium nitrate and ammonia carbonate, with an absorption of about 3,000 heat-units per equivalent of nitrate. The ammonia carbonate passes off from the solution by evaporation and diffusion, and, in an unlimited atmosphere, the ammonia separates from the carbonic acid, and becomes oxidized into ammonia nitrate under the same influences as those which have effected the first oxidation; then, by repetition of this series of changes, the whole of the ammonia becomes converted into potassium nitrate.

The transformation of ammonia nitrate into calcium or magnesium nitrate is effected by means of similar reactions, with this difference, however, that the double decompositions may take place between the ammonia nitrate and the earthy carbonates held in solution by carbonic acid. Magnesium carbonate may also be held in solution by forming a double salt with the ammonia carbonate.

Disregarding the intermediate transformations, the heat disengaged by the nitrification of ammonia into potassium nitrate—

$$2NH_3 + 8O + (CO_3K_2 + nAq.) = 2(NO_3K + nAq.) + 3H_2O + CO_2.$$

may be directly calculated, and is found to amount to 221,000 heat-units.* This number differs very little from that corresponding to the formation of dilute nitric acid. The excess, about 4,000 heat-units, represents the difference between the heat-of-combination of dilute nitric acid and that of carbonic gas with potassa. It is from this again evident that natural nitrification, once provoked, can be continued under the same conditions, namely, the presence of alkaline or earthy carbonates, without the assistance of any external energy.

This assistance, however, is not wanting, for the oxidation of the

* Ammonia and carbonic acid both gaseous; potassium carbonate and nitrate both in solution.

organic matters, nitrogenous and non-nitrogenous, proceeds simultaneously with that of the ammonia derived from them, and adds to the quantity of heat disengaged. The fact that the presence of an alkali, free or carbonated, facilitates the absorption of oxygen by organic matter, is also explicable by thermic considerations. For the oxidation of organic matters engenders acids, the formation of which, and their simultaneous combination with the alkali, disengage more heat than would be liberated by the formation simply of the same acids in the free state. For example, the change of alcohol into potassium acetate disengages 14,000 heat-units more than its change into free acetic acid.

The disengagement of heat is further added to by the oxidation itself becoming often more profound under the influence of this additional work; such is the case with alcohol. It is necessary to raise the temperature of the alcohol considerably, to cause it by itself to absorb oxygen, and produce aldehyde and acetic acid. But by placing the alcohol in presence of an alkali, as well as of oxygen, it is oxidized gradually at ordinary temperatures, and forms not only acetic acid but even oxalic acid, or rather an oxalate. Now the metamorphosis of alcohol into potassium oxalate in solution disengages 164,000 heat-units more (per equivalent of alcohol) than its metamorphosis into acetate.

An analogous condition of things can be shown to be produced in nitrification, upon the hypothesis that nitrates can result from the direct oxidation of nitrogenous organic matters. It will be sufficient, to take a well defined example, to make an approximate calculation of the heat disengaged in the nitrification of hydrocyanic acid, or rather, of potassium cyanide, a calculation of some interest in itself, on account of the frequent presence of cyanides in bricks and other nitrifiable materials.

From the equation—

$$2(CNK + nAq.) + 10O = 2(NO_3K + nAq.) + 2CO_2,$$

the calculation can be made as follows:—

1st. Separation of alkali cyanide into potassa and hydrocyanic acid, all being in solution:

Andrews, −7,200 heat-units; Thomsen, −5,600; the author's unpublished experiments, −5,920; number adopted . .	− 6,000

2nd. Separation of the water and the acid, both liquid:

From the author's experiments, for a dilute solution	− 800

3rd. Oxidation of pure and liquid hydrocyanic acid:

$$2CHN + 5O = 2CO_2 + H_2O + N_2.$$

From author's experiments	+ 332,000
4th. $N_2 + 5O + H_2O + n$Aq. $= 2NO_3H + n$Aq.	+ 55,400
5th. Union of dilute nitric acid with dissolved potassa	+ 29,600
Total heat disengaged	+ 410,000

This quantity refers to the nitrification of potassium cyanide, with the formation of dissolved nitre; it is nearly double that of the heat disengaged in the nitrification of ammonia at the expense of dissolved potassium carbonate; such an excess is in great part due to the oxidation of the carbon, and will probably be likewise found in the oxidation of other nitrogenous organic matters.

Gaseous hydrocyanic acid* would disengage 429,000 heat-units in furnishing two equivalents of potassium nitrate; ammonia hydrocyanide in solution† would disengage 317,000 heat-units for two equivalents of nitre formed.

All three numbers exceed that which corresponds to the oxidation of ammonia alone (221,000); it may, therefore, be accepted that nitrification must be facilitated by the simultaneous oxidation of the carbon contained in the organic substance.

E. D.

Absorbent Power of Red Phosphorus. By F. Sestini.‡

The solid residue, partly red-brown, partly orange-coloured, which is obtained in the preparation of ethyl iodide by the process of Frankland, or of E. Kopp, consists of amorphous phosphorus, together with ordinary phosphorus, iodine, and traces of phosphoric acid, these impurities, especially the iodine, being retained with considerable tenacity. It may be completely freed from ordinary phosphorus by eight successive treatments with boiling ether; but on treating the remainder with a hot alkaline ley, it is transformed, with evolution of phosphoretted hydrogen, into a black substance, and the liquid takes up a considerable quantity of iodine. A sample of red phosphorus obtained as above was found to contain 3·369 p. c. iodine, although,

* The author has found the heat of vaporization of this acid equal to 5,700 heat-units (for one equivalent).

† The author has found that the union of hydrocyanic acid with ammonia, both in solution, disengages 1,600 heat-units.

‡ Gazzetta chimica Italiana, i, 323—326.

before being treated with ether, it had been left for a fortnight under water.

This strong *chemical adherence* exerted by red phosphorus is similar to that of gum-benzoin for sublimed benzoic acid, and may be compared with the absorbent power exerted by carbon and other bodies in the porous state. This view is supported by the observation of Brodie, that a mixture of red phosphorus and iodine may be distilled without alteration.

Further evidence of the *chemical adherence* of red phosphorus to metalloïds was obtained in treating the above-mentioned residue of the preparation of ethyl iodide with carbon bisulphide, for the purpose of freeing it from ordinary phosphorus. On digesting the remaining substance with boiling potash-ley, the liquid took up, not only iodine, but likewise sulphur, in the form of sulphide, which must have been derived from the bisulphide of carbon: hence it appears that this compound, in contact with red phosphorus at the boiling heat, suffers an incipient decomposition, whereby a sulphuretted substance is produced, which remains adhering to the red phosphorus.

The absorbent power of red phosphorus for iodine may be easily demonstrated as a lecture-experiment by placing some carbon bisulphide, coloured red-violet by iodine, in a test-tube, and shaking it with red phosphorus previously exhausted with water and ether; in a few seconds the liquid becomes perfectly colourless.

Red phosphorus is also capable of abstracting certain organic bodies from liquids in which they are dissolved. Thus on briskly agitating 2 or 3 grams of it with 10 c.c. of an ethereal solution of aniline-red (containing 0·5 grm. of the colouring matter in 100 c.c. of ether), the liquid will be wholly or almost wholly decolorised in ten or fifteen minutes. The process is one of simple absorption, the aniline-red not being decomposed or altered in any way.

Red phosphorus, as observed many years ago by Personne,* is slowly oxidized and acidified by exposure to moist air. From more recent observations by Prof. Guerri, of Florence,† it appears that the products of this slow oxidation are phosphorous and metaphosphoric acids, and that the latter acid is also formed by treating red phosphorus with dilute nitric acid, or with chlorine in presence of water.

H. W.

The Atomic Weights of Cobalt and Nickel. By RICHARD H. LEE.‡

THE author introduces the subject by reviewing at considerable length the labours of those chemists who have from time to time undertaken

* Compt. rend., xlv, 113. † Sperimentale, Settembre, 1864.

‡ Am. J. of Sci. [3], ii, 44—52.

the determination of the atomic weights of cobalt and nickel. The following is a brief summary of the results obtained, reduced to the modern scale of atomic weights:—

Cobalt.		*Nickel.*	
1826. Rothoff	59·10	1826. Rothoff	59·20
1857. Schneider	60·00	1852. Erdmann and	58·20 to
1857. Marignac	58·93	1852. Marchand	58·60
	58·78	1857. Schneider	58·04
1859. Dumas	59·08	1857. Marignac	58·40 to 59
1863. Russell	58·74	1859. Dumas	59·028
1866. Sommaruga	59·93	1863. Russell	58·74
1867. Winkler	58·99	1866. Sommaruga	58·026
1869. Weselsky	58·96	1867. Winkler	59·054
1871. *Lee*	59·10	1871. *Lee*	58·01

The methods adopted by the author for the determination of the atomic weight of cobalt do not differ in principle from those of Weselsky and Sommaruga. Cobalticyanides of alkaloïds having high atomic weights, and forming perfectly definite and highly crystalline double cyanides, were prepared. In these salts the water of crystallisation was directly determined, and afterwards the percentage of cobalt. From the numbers so obtained the atomic weight was calculated. The practical details were as follows:—

Commercial cobaltic oxide was first converted into an impure sulphate, and the solution of the salt treated with a current of sulphuretted hydrogen, to remove all metals precipitable by that gas. The iron in the filtrate was peroxidised with chlorine, and afterwards removed, together with manganese, by the addition of barium carbonate. The solution was then treated with a large excess of barium carbonate, and cyanhydric gas passed into the liquid, until the whole of the cobalt was converted into cobalticyanide of barium.

The nickel, as well as traces of iron and manganese, still present in the solution, were removed by boiling with mercuric oxide, and the mercury having been removed from the filtrate by sulphydric gas, the solution of cobalticyanide of barium was regarded as chemically pure.

The brucine and strychnine salts were prepared by decomposing the sulphates of these bases with the above solution of cobalticyanide, and repeatedly crystallising the salts formed. The crystals of both alkaloïds closely resembled each other; they were but slightly soluble in water, crystallising almost completely from their solutions on cooling. The analysis was effected by carefully burning the salt in a platinum crucible, first in air, then in oxygen, and finally reducing the oxide to the metallic state by a current of pure hydrogen. The cobalt was then weighed.

The atomic weight of this metal calculated from the mean results of six analyses of the strychnine salt, was fixed at 59·05, and from a similar number of analyses of the brucine salt, at 59·15.

As a check upon the foregoing numbers, another series of experiments was made by igniting the chloride of purpureo-cobalt in a current of hydrogen. The atomic weight calculated from the percentage of metal obtained was found to be 59·09.

The determination of the atomic weight of nickel was conducted in a manner precisely similar to that which has already been described in the case of cobalt. The double cyanides of nickel with strychnine and brucine were prepared, and the percentage of nickel in both salts was ascertained.

The constitution of the salts was represented thus :—

Brucine compound, $Ni_3Cy_{12}(C_{23}H_{26}N_2O_4)_6H_6 + 10H_2O$.
Strychnine ,, $Ni_3Cy_{12}(C_{21}H_{22}N_2O_2)_6H_6 + 8H_2O$.

The analyses of the brucine compound gave the number 57·98 as the mean atomic weight, while from the strychnine salt the mean number was calculated at 58·04.

As the result of the foregoing analyses, the atomic weight of cobalt, calculated from eighteen determinations by two distinct processes, is 59·10. The atomic weight of nickel from twelve determinations, is 58·01.

J. W.

On the Corrosion of Copper Plates by Nitrate of Silver. By J. H. Gladstone and Alfred Tribe.*

In some recent experiments in chemical dynamics, the authors had occasion to study the action of nitrate of silver on copper plates in various positions. They observed that, when the plate was vertical, there was rather more corrosion at the bottom than at the top. This is easily accounted for by the upward current, which flows along the surface of the deposited crystals, and necessitates a movement of the nitrate of silver solution towards the copper plate, especially impinging on the lower part.

It was found also that, when the copper plate was varnished on one side, it produced rather more than half the previous decomposition, and was most corroded at the edges of the varnish. By making patterns with the varnish, this edge action became very evident. This was explained by the fact that the long crystals of silver, growing out from the copper at the borders, can spread their branches into the open space at the side, and so draw their supply from a larger mass of solu-

* Chem. News, xxiv, 76.

tion, than the crystals in the middle can do; and increased crystallisation of silver means increased solution of copper.

This was proved by making the varnish form a perpendicular wall, instead of a thin layer, when the greater corrosion was not obtained. In a plate completely surrounded with liquid, the greatest growth of crystals is also evidently from the angles. It was likewise observed, that if a vertical plate be immersed, the lower part in nitrate of copper, and the upper part in nitrate of silver, there is greater corrosion about the point of junction; this was attributed to the greater conduction of the stronger liquid.

J. W.

The Reduction of Chloride and Iodide of Silver by Hydrogen. By A. VOGEL.*

The following are suggested as instructive lecture experiments:—

Pass hydrogen over silver chloride heated by a gas flame in a combustion-tube drawn at its anterior end nearly to a point: the chloride will be quickly reduced, with formation of hydrochloric acid.

Next replace the hydrogen by coal gas: the chloride, as before, will be reduced, and a part of the hydrochloric acid, by combining with ammonia in the gas, will form ammonium chloride, which will appear on the cool narrow part of the tube.

Now substitute silver iodide for chloride, and again pass hydrogen through the tube, the source of heat being the same: reduction does not take place; in fact, hydrogen only partly reduces silver iodide, even at a white heat.

These experiments show that hydrogen decomposes the iodide with far greater difficulty than it does the chloride, which agrees with the author's previous observations on the decomposition of these compounds by fusion with potash.

A. T.

On a New Class of Platinum-compounds. By P. SCHÜTZENBERGER.†

A MIXTURE of dry chlorine and carbonic oxide passed over platinum-black contained in a glass tube heated to 300°—400° over a gas-flame yields a considerable quantity of chlorocarbonic oxide, while at the same time a yellow flocculent body containing platinum condenses in the cool part of the tube. But the temperature produced in this way is too high, for the platinum contracts considerably, and its full action on the gases is not obtained. The process succeeds better, and gives a

* N. Repert. Pharm., xx, 385.

† J. pr. Chem. [2], iv, 159—171; from Ann. Chim. Phys. [4], xxi, 350.

much higher yield when the following modification of it is adopted. A straight, tolerably stout glass tube, about 1 metre in length, and 1—1·5 cm. in diameter, is fixed in an oil-bath 30 cms. long, furnished with lateral apertures. The part of it within the oil-bath is filled with spongy platinum retained in position by two plugs of asbestos. The further end of the tube is allowed to project 50 cms. beyond the bath, and is connected with a small wash-bottle provided with a tube for conveying away excess of chlorine. The fore-part of the tube, 2—3 cms. long, is connected with the chlorine and carbonic oxide generators. The apparatus being thus arranged, the temperature of the oil-bath is brought to 240°—250°, and chlorine alone sent through the tube until no more of it is absorbed. At this temperature only platinous chloride is formed. The current of chlorine is then replaced by one of carbonic oxide, either pure, as obtained from its solution in cuprous chloride after washing with potash-solution, or, as produced from oxalic and sulphuric acids, mixed with an equal volume of carbonic acid, this gas being without action, and serving advantageously to carry forward the vapour of the platinum compound. In this way it is easy to obtain in an hour about 20 grms. of the solid compound, partly in the form of bright yellow needles, partly as a yellow crystalline incrustation, and partly as yellow flocculi, lining the more remote parts of the tube. Close to the oil-bath, it is completely fused, forming a red, transparent ring, which, on cooling becomes a yellow crystalline crust, easily removable from the tube. The entire product must be carefully excluded from moisture, as the least trace of water is sufficient to blacken it by causing a separation of metallic platinum.

Both its analysis and the determinations of its melting point prove it to be a mixture. It is, besides, not homogeneous in appearance, exhibiting perfectly white crystals intermingled with the yellow ones, and when first heated in a tube to 150°, it yields a sublimate of colourless needles in small quantity, not increased by a continuance of the same temperature.

It dissolves in boiling dry carbon tetrachloride (boiling point 76°), and separates out again almost completely on cooling in the form of fine yellow needles. After decanting their mother-liquor and drying them at a temperature of 50° in a current of dry carbonic acid, the crystals obtained by the first treatment of the crude product with the tetrachloride are found to have the composition expressed by the formula, $C_3O_3Pt_2Cl_4$. A second and a third boiling out with this solvent yield diminishing quantities of crystals, and it becomes plain that the residue consists of a much less soluble body than that which first dissolved out. Crystals deposited from the last-employed portions of the carbon tetrachloride have a composition which may be expressed either by $C_2O_2PtCl_2$ or by $C_4O_4Pt_2Cl_4$. The crude product must therefore consist of a mixture

of the bodies $C_2O_2PtCl_2$ and $C_3O_3Pt_2Cl_4$ in varying proportions. The following experiments leave no doubt as to the correctness of this conclusion:—

(1.) When the crude product (mean percentage of platinum 61·8; melting point, 135°) is heated in a test-tube provided with a delivery-tube, to 250°—260°, an evolution of pure carbonic oxide takes place with effervescence, and after this has ceased, an orange-red transparent liquid remains, which on cooling is converted into a mass of beautiful, long, golden-yellow needles. To obtain the new product in the pure state, all the liberated carbonic oxide must be carefully expelled from the tube by a current of carbonic acid, and the product then sublimed at a temperature of 250° in an atmosphere of the latter gas. If this be not done, it takes up carbonic oxide again as it cools. It has the composition, $COPtCl_2$.

(2.) If some of the crude product is maintained for an hour at a temperature of 150° in a current of pure carbonic oxide, it absorbs a considerable quantity of this gas. The fused body, at first orange coloured, becomes pale yellow, sublimes in the form of white needles, and on cooling solidifies to a mass of nearly colourless, long needles. Thus changed, it has the composition expressed by the formula, $C_2O_2PtCl_2$.

These experiments prove the existence of two compounds, $COPtCl_2$ and $C_2O_2PtCl_2$, not described in the author's previous paper. They may be called carbonyl chloroplatinite and dicarbonyl chloroplatinite. They are readily convertible into each other, the former into the latter by saturating it with carbonic oxide at 150°, and the latter into the former by heating it to 250° in a current of some indifferent gas. The intermediate compound, $C_3O_3Pt_2Cl_4$, resulting from the union of one molecule of carbonyl-platinous chloride with one of dicarbonyl-platinous chloride, cannot be regarded as a mixture only of these bodies, inasmuch as its melting point is below that of either of them. From its composition it may be called sesquicarbonyl-chloroplatinite. It can be obtained by keeping $C_2O_2PtCl_2$ at 210° until carbonic oxide ceases to be evolved; by subliming either $C_2O_2PtCl_2$ or $COPtCl_2$ at a temperature of 250° in a current of carbonic oxide; or by passing carbonic oxide over platinous chloride, or phosgene gas over spongy platinum at the last named temperature. But in none of these ways can it be obtained unmixed with a little $C_2O_2PtCl_2$. It can, however, be got in the pure state by treating the product with carbon tetrachloride, as already described.

There are, thus, three compounds of carbonic oxide with platinous chloride—carbonyl chloroplatinite, dicarbonyl chloroplatinite, and sesquicarbonyl chloroplatinite.

Carbonyl Chloroplatinite, $COPtCl_2$. A solid, golden-yellow or orange-

yellow substance, melting at 195° to an orange-red transparent liquid, subliming at 240° in a current of carbonic acid in the form of long golden-yellow needles, and decomposing at a high temperature (300°—400°) into platinum and phosgene. It is soluble in hot carbon tetrachloride and crystallises out again on cooling.

Water decomposes it in the cold into hydrochloric acid, carbonic acid and platinum, but this decomposition is not complete. The platinum-black retains 2—3 per cent. of chlorine, and the liquid filtered off from it, which is colourless, still contains platinum, some of which can be precipitated by treatment with sulphuretted hydrogen, but the rest of which can only be obtained by evaporation and ignition of the filtrate. Alcohol decomposes it, with separation of platinum and formation of chlorocarbonic ether.

Dicarbonyl-platinous Chloride or Dicarbonyl Chloroplatinite, $C_2O_2PtCl_2$. A solid body, light yellow in large quantities, but almost colourless when sublimed; it melts at 142° to a yellow, transparent liquid, which solidifies on cooling to a mass of beautiful, long needles. It sublimes slowly at 150° in a current of carbonic oxide, in the form of white needles. At 210° carbonic oxide is evolved, the melting point falls, and the intermediate compound, $C_3O_3Pt_2Cl_4$, is obtained. When it is heated to 150° in a current of dry chlorine, chlorocarbonic oxide is given off, and a dark-red liquid remains, which only towards 120° solidifies to an apparently amorphous, red mass, isomeric or polymeric with carbonyl chloroplatinite. It is decomposed by water into hydrochloric acid, carbonic acid, carbonic oxide, and platinum:

$$C_2O_2PtCl_2 + H_2O = 2ClH + Pt + CO + CO_2.$$

Sesquicarbonyl Chloroplatinite, $C_3O_3Pt_2Cl_4$. An orange-yellow, solid body, melting at 130°. It evolves carbonic oxide at 250°, and is converted into $COPtCl_2$. Water and alcohol both decompose it, with separation of platinum.

It is worthy of remark that the compounds $C_2O_2PtCl_2$ and $C_3O_3Pt_2Cl_4$, which both show a tendency, under the influence of heat, to evolve carbonic oxide and pass into the more stable compound, $COPtCl_2$, are permanent in an atmosphere of carbonic oxide, even at temperatures at which they are decomposed in presence of an indifferent gas. These results are in accordance with the general phenomena of dissociation.

In the analysis of these bodies, the platinum was determined by adding water and a little ammonia, to a weighed portion of the substance in a platinum crucible, cautiously evaporating to dryness and igniting. The chlorine was determined either by the lime method usually employed with organic chlorine-compounds, or by decomposing the substance with ammoniacal water, separating the platinum by filtration, and precipitating with silver nitrate.

The constitution of the above described compounds can be easily accounted for by the following representations:—

Carbonyl chloroplatinite.

$$PtCl_2{=}CO$$

Dicarbonyl chloroplatinite.

$$PtCl_2\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle$$

Sesquicarbonyl chloroplatinite.

$$PtCl_2\left\langle\begin{matrix}CO{-}PtCl_2\\CO{-}CO\end{matrix}\right\rangle$$

In carrying out these researches, there has been occasion to study a hitherto undescribed compound of platinic chloride with alcohol, which is formed by evaporating a solution of platinic chloride in absolute alcohol at ordinary temperatures over sulphuric acid in a vacuum. To obtain it quite dry it must be left for 10 or 15 days in an almost perfectly dry vacuum. It is a reddish-yellow, extremely deliquescent body, which begins to decompose even at 50°. Subjected to analysis it gave numbers leading to the formula, $PtCl_4.2C_2H_6O$.

E. D.

On the Composition of Tantalic and Niobic Compounds. By C. RAMMELSBERG.*

FROM the examination of six different tantalites it was found that tantalite is a mixture of isomorphous ferrous (manganous) tantalate and niobate; containing among other things a considerable proportion of tin. The stannic acid in tantalite is not free, but combined with iron (manganese). Tantalite consists of the molecules $FeTaO_6$, $FeNb_2O_6$, and FeS_nO_3.

The columbites examined were mixtures of the same ground-constituents of tantalum and niobium, in which tantalum was to niobium as 1 : 2, 3, 4, 7, 8, and 38.

The examination of various pyrochlores showed that they were mixtures of sodic fluoride with niobic and titanic salts of bivalent metals (Th,Ce,Ca,U,Fe,Mn).

C. H. G.

On the Platinocyanides and Tartrates of Beryllium. By F. TOCZYNSKI.†

THE author finds that the best method of freeing beryllia from alumina and ferric oxide is to add to the solution of beryllia in ammonium carbonate, sufficient ammonia to produce a small precipitate, in which after some standing, the impurities are deposited.

Beryllia, after ignition, loses the power of decomposing ammonia

* Chem. Centr., 1871, 511. † Zeitschr. f. Chem. [2], vii, 275.

salts by boiling with their solutions; this property may serve as a means of separation from magnesia. In presence of tartaric acid, beryllia is not precipitated by ammonia: cane-sugar, grape-sugar, and glycerin are less effective.

Beryllium cyanide seems capable of existing only in very dilute solution: barium cyanide decomposed by beryllium sulphate, gives a solution containing traces only of beryllium cyanide. *Beryllium platinocyanide*, $BePtCy_4$(Be = 9·23), was obtained by the decomposition of barium platinocyanide by means of beryllium sulphate, and purified by solution in alcohol and ether. Below 30°, the salt contains water and is golden-yellow; at 30° it becomes orange coloured; at a higher temperature it appears red and green.

Beryllium-magnesium platinocyanide, $BeMg_2Pt_3Cy_{12} + 16H_2O$, crystallises from a mixture of magnesium and beryllium platinocyanides, in colourless crystals. At the same time, other double compounds, which are dichroic, are produced.

Beryllium tartrates. On evaporating a solution of 2 mols. cream of tartar and 1 mol. beryllium hydrate, some cream of tartar is first deposited, and then peculiar crystalline growths somewhat resembling yeast-cells; this is a basic double tartrate, whose composition is expressed by $C_8H_4H_2K_2Be_2O_{12}$. Another tartrate, $C_8H_2Be_4K_2O_{12} + 3H_2O$, is produced by boiling solution of cream of tartar with excess of beryllia. Double tartrates of antimony and beryllium were obtained by boiling together trioxide of antimony, beryllia, and tartaric acid: they are non-crystalline substances.

W. H. D.

Mineralogical Chemistry.

Ceruleolactine and Variscite. By T. Petersen.*

The author gives the former name to a new mineral found in the Rindsberg Mine, at Katzenellbogen, in Nassau, in a bed of brown iron ore. It occurs in threads and veins, and in clefts, in botryoïdal and reniform masses. In colour it is dull and usually milky-white, merging into the pale blue of some copper compounds; occasionally the tint is still more marked; and again, when in thin threads it is almost colourless. In structure it is crypto- or microcrystalline; the fracture is conchoïdal, irregular to hackly; it is slightly translucent, somewhat greasy to the touch, and has a white streak. The specific gravity of this mineral is 2·593, the hardness 5; it is readily soluble in mineral acids, and easily taken up by caustic potash or soda. It has the following composition: silicic acid 1·82; phosphoric acid

* Jahrbuch für Mineralogie, 1871, 353.

36·33; alumina 35·11; iron oxide 0·93; copper oxide 1·40; lime 2·41; magnesia 0·20; water 21·23; with traces of zinc oxide and fluorine. If those constituents, which appear to be accidental be left out of consideration, and the remaining percentages be together raised to 100, we get the following numbers:

		$3Al_2O_3.2P_2O_5.10H_2O$.
Phosphoric acid.....	37·04	36·74
Alumina.....	39·34	39·97
Water.....	23·62	23·29
	100·00	100·00

The numbers in the second column are the percentages of the aluminium phosphate, corresponding to the analytical numbers. It may be well to place beside the formula of ceruleolactine those of calaite and wavellite:—

$\underbrace{2Al_2O_3.P_2O_5.5H_2O}_{\text{Calaite.}}$. $3Al_2O_3.2P_2O_5.10H_2O$. $\underbrace{3Al_2O_3.2P_2O_5.12H_2O}_{\text{Wavellite.}}$.

Variscite. This mineral was found by Breithaupt at Messbach, near Plauen in the Saxon Voigtland, with quartz in siliceous shale. Its similarity to ceruleolactine made it desirable that it should be further investigated. It is amorphous, distinctly crystalline, more or less translucent, usually of a pale apple-green colour, and often colourless; somewhat brittle, with an uneven conchoïdal fracture and white streak. It dissolves somewhat easily in mineral acids, even after ignition.

Variscite has the following composition:—

	P_2O_5.	Al_2O_3.	Cr_2O_3, Fe_2O_3, and FeO.	MgO.	CaO.	H_2O.	
Analysis.....	44·05	31·25	1·21	0·41	0·18	22·85	= 99·95
Calc. for $Al_2O_3,P_2O_5,4H_2O$.	44·80	32·49	..	..	..	22·71	= 100

Variscite, $Al_2O_3.P_2O_5.4H_2O$, differs but little in properties and composition from that variety of aluminium phosphate which Damour found in wrought forms in Celtic graves, and to which he gave the name of callais (callainite) $Al_2O_3.P_2O_5.5H_2O$.

W. F.

Sal-ammoniac, from Vesuvius. By A. KENNGOTT.*

IN a crystalline crust of this substance covering a brown porous lava ejected in 1869, the author found crystals, some 3 mm. in diameter, exhibiting ∞O . 202. The latter faces are smooth and very lustrous; the former pitted, colourless, transparent and of a glassy lustre.

W. F.

Crystalline Compounds of Lead Antimonite and Antimoniate from Constantine. By M. FLAJOLOT.†

ABOUT 60 kilom. south of Bona, and near a thermal spring at Gebel Nador, much frequented by the Arabs, is a bed of calamine in nummulitic limestone. The drusy cavities of the ore are covered with numerous crystals, apparently of a new species. One of these minerals occurs in transparent tabular crystals of a greyish brown colour, with a grey streak, a hardness about 3, and a specific gravity of 7·02. When analysed they were found to be composed of 44 per cent. Sb_2O_3 and 56 PbO. The author proposes the name of Nadorite for this substance.

A portion of these tabular crystals, by exposure to the atmosphere, while they retain their original form, have been converted into an orange-coloured substance that in the tabular habit of its crystals strongly recalls Wulfenite. It has the following composition:—

Sb_2O_3.	Sb_2O_5.	CO_2.	PbO.	H_2O.
4·80	35·50	4·20	51·50	4·00 = 100·00

The quantities of antimonic acid and carbonate of lead indicate the formula $Sb_2O_5.PbCO_3.PbH_2O_2$. The author is, however, of opinion that this substance may be a mixture. An amorphous substance occurring on the calamine consisted of antimonic acid 63·50 per cent., iron oxide 31·40 per cent., and water 5·10 per cent., which corresponds with the formula $Sb_2O_5.Fe_2O_3.\frac{3}{4}H_2O$.

W. F.

Desmin. By E. E. SCHMID.‡

OF the equivalent ratios, calculated from the majority of the analyses of this mineral which have yet been published, while that of protoxides to sesquioxides is 1 : 1, that of silica to total base is usually less than 3 : 1. This is ascribed to the occurrence of other zeolites with this mineral. A specimen from Stromö contained an amount of silica, varying from 52 to 55 per cent. A closer inspection showed that the

* Jahrbuch für Mineralogie, 1871, 405. † Ibid., 1871, 406.
‡ Jahrbuch für Mineralogie, 1871, 408.

bundles of fibrous crystals were made up of two mineral varieties of different habit.

The former are foliate, radiate, lustrous, translucent, and of a pale red colour; the others finely radiate, dull, almost opaque and colourless. These bundles meet and often distinctly interpenetrate, in which case it will be remarked that the foliated bundles are the more recent formation, by their displacing the finely rayed bundles or occupying the interstices between them. There also occur, though but rarely, plates of stilbite having a pearly lustre. By carefully isolating the foliated bundles, a homogeneous material was obtained, having a specific gravity of 2·16 and a hardness of 3·5. It completely dissolves in acid, with subsequent gelatinisation. The fine powder dried at 100° had the composition—

		Oxygen.	
Silica	56·879	30·234	11 695
Alumina, with a trace of iron protoxide	16·698	7·781	3·00
Lime	7·694	2·198	0·991
Magnesia	0·028	0·011	
Soda	1·389	0·362	
Water	17·245	15·331	5·911
	99·933		

These numbers correspond very completely with the formula of desmin, the chief discrepancy being in the proportion of water. The powder of desmin lost, after long exposure to a dry current of air, 0·430 per cent., and suffered no further diminution in weight till the boiling point was reached, when it lost 1·634 per cent. in five hours. Above this temperature, the loss of water rapidly increases. Another specimen of a zeolite, of similar habit, from Waagö, having the same hardness and density, and showing the same reactions before the blowpipe, had the following composition:—

		Oxygen.	
Silicic acid	56·300	30·025	10·962
Alumina	17·633	8·217	3·00
Lime	7·497	2·142	0·989
Magnesia	0·051	0·020	
Soda	2·094	0·546	
Water	17·362	15·435	5·635
	100·937		

The pulverised mineral was dried in the water-bath, and consequently no longer contained its entire proportion of water. At ordinary temperatures it gave off water to some degree, readily, however, at the

boiling point; in the former case 0·184 per cent. in nine hours, and in the latter 1·822 per cent. in five hours. The numbers vary but little, and only as regards the silicic acid, from those given by normal desmin, and approximate to those mentioned above of a mixture of desmin with mesolite. In short, the greater part of the specimens of desmin that have been examined, appear to have been mixed with mesolite or another fibrous zeolite, with a lower percentage of silica.

W. F.

Mesolite. By E. E. Schmid.*

The investigations of Schmid support the view that mesolite is to be regarded as a distinct mineral species. He examined three specimens, two from Iceland (I and II), the former consisting of radiate bundles terminated in free crystals, which exhibit the combination of the clinorhombic prism with the clinopinacoïd and the complete pyramid, while the latter and that from Stromö (III) are finely radiate, the ends not being free. At ordinary temperatures they lose but little water, probably hydroscopic, the quantity not being greatly increased when the heat is raised to 100°. Above the boiling point the loss increases, and by a gentle incandescence continued for half a hour, all the water passed off, amounting to 12·943, 13·190, and 13·355 per cent. respectively. Coarse fragments, after lying two days in acid, show signs of gelatinisation. The portions analysed were dried at 100°, and had consequently lost somewhat more than the hygroscopic water; the results were:—

	I.			II.			III.		
		Oxygen.	Oxygen ratios.		Oxygen.	Oxygen ratios.		Oxygen.	Oxygen ratios.
Silicic acid.....	46·583	24·842	5·802	47·133	25·136	6·102	47·404	25·281	6·107
Alumina, with a trace of iron oxide.....	27·566	12·845	3·00	26·520	12·358	3·00	27·049	12·605	3·00
Lime.....	9·105	2·602	0·836	10·365	2·961	1·006	9·163	2·618	0·919
Magnesia.....	0·076	0·030		0·025	0·010		0·058	0·023	
Soda.....	3·638	0·948		4·501	1·173		4·689	1·222	
Specific gravity..	2·18	..	..	2·18	..	..	2·16	..	..

The ratios of the constituents, with the exception of the water, are those of labradorite. The amounts of water in these three new specimens show as little uniformity as those of earlier analyses, and it is this point, in fact, that has made the recognition of mesolite as a dis-

* Jahrbuch für Mineralogie, 1871, 406.

tinct mineral species, a matter of doubt. Fuchs held that the water percentage was dependent on those of soda and lime, and considered mesolite to be formed of scolecite and natrolite as proximate constituents. If then the oxygen of the soda be $\frac{1}{m}$ of that of the total protoxides, the water will, on this assumption, be $3 - \frac{1}{m}$, and the formula:—

$$2\left(1 - \begin{matrix}\frac{1}{m}\dot{C}a \\ \frac{2}{m}\,Na\end{matrix}\right\} Si + Al_2Si_3 + 2(3 - \tfrac{1}{m})\dot{H}.$$

The amount of water calculated from this formula accords very satisfactorily with that found by experiment. In any case the new view is preferable to the one advanced by Rammelsburg, that scolecite and mesolite are similarly constituted.

W. F.

On Ralstonite, a New Fluoride from Arksut-Fiord. By G. J. Brush.*

This mineral was found, in connection with several other fluorides, during the recent examination of Greenland cryolite. The crystals are octohedral, and in most cases very minute, but are occasionally found of one to one and a-half millimetres in diameter. They are often implanted on crystals of thomsenolite, and also apparently intercrystallised with this species, making it exceedingly difficult to separate a specimen sufficiently pure for analysis. The mineral is colourless to white, with a vitreous lustre; its hardness is equal to 4·5 sp. gr. 2·4.

The preliminary examination, by heating in a small tube, showed unmistakeably the presence of fluorine; the sides of the tube were etched, and the moisture reacted acid. Heated with cobalt solution in the platinum forceps, the mineral assumed a bright alumina-blue, and when fused with microcosmic salt, dissolved readily, producing a colourless bead.

On account of the intimate manner in which the new mineral was associated with thomsenolite, a qualitative analysis only was attempted. 30 milligrams, selected with care to ensure purity, were decomposed in platinum with sulphuric acid, and heated until all hydrofluoric acid was expelled; the solution was then examined and found to contain alumina, with traces only of lime and soda. The filtrate, from which alumina was separated, afforded, on evaporation to dryness, a minute residue, which, when examined with the spectroscope, showed only the sodium and calcium lines.

* Am. J. of Sci. [3], ii, 30.

The above analysis showed that the mineral under examination was essentially a hydrous fluoride of aluminium, while its isometric form, and its infusibility, were sufficient to distinguish it from all other fluorides yet described, as occurring at the cryolite locality in Greenland.

J. W.

On Three Masses of Meteoric Iron. By J. W. MALLET.*

THE author having recently obtained possession of three large masses of meteoric iron, of 56 lbs., 36 lbs., and $3\frac{1}{2}$ lbs. weight respectively, submitted them to examination and analysis.

All three specimens presented the same general appearance. They were of a very irregular pear shape, one end of each mass being larger and more rounded than the other. On the exterior they were covered with a dark brown crust, consisting essentially of hydrated ferric oxide, which varied from about one-eighth to one-third of an inch in thickness. The masses were of course magnetic, and on examination gave evidence of feeble magnetic polarity, with multiple poles. The interior structure of the iron was compact, and highly crystalline, of much the same general character throughout; but a few small grains and streaks of a brownish-yellow mineral were noticed, which on being picked out and examined proved to be *troilite*. Minute fissures also were observed, running through several portions of the metal, from which a watery liquid containing chlorine exuded. Traces of the Widmanstättian figures might be detected upon a polished surface, even without the aid of an acid, and when the iron had been etched with nitric acid, the markings became exceedingly distinct and beautiful. In all three specimens, upon the principal cut surfaces, narrow, well defined bands of alternate nickel-iron and Schreibersite were visible, the alternations sometimes running parallel, but more often intersecting each other at angles of 60°, 90°, or 120°.

The iron was not passive, but very easily rendered so by nitric acid.

The following are the results of chemical analysis, No. 1 representing the largest, and No. 3 the smallest specimen:—

* Am. J. of Sci. [3], ii, 10—15.

	No. 1.	No. 2.	No. 3.
Specific gravity at 15° C.....	7·853	7·855	7·839
Iron.....	88·706	88·365	89·007
Nickel.....	10·163	10·242	9·964
Cobalt.....	·396	·428	·387
Copper	·003	·004	·003
Tin	·002	·002	·003
Manganese	trace	—	trace
Phosphorus.....	·341	·362	·375
Sulphur	·019	·008	·026
Chlorine	·003	·002	·004
Carbon	·172	·185	·122
Silica	·067	·061	·056
	99·872	99·659	99·947

Particular attention is directed to the presence of a small quantity of tin in the present specimens, inasmuch as it has been stated that this metal seldom or never accompanies meteoric iron. The author is of opinion that the chlorine is not an essential constituent of the original masses, but has been derived from the soil in which the iron has lain embedded. No chlorine could be detected in a specially selected solid piece, of some 50 grams weight, taken from a part of No. 1, destitute of fissures and flaws.

The siliceous residue, although returned as silicic acid, appeared upon examination to have existed partly in combination as silicide of iron. J. W.

On the Magnesium Sulphate Springs of Hunyadi János near Ofen. By ALOIS MARTIN.*

ANALYSES of the waters from six wells, all from the same stratum, have yielded the following numbers in one thousand parts by weight:—

Date of analysis	Summer 1870.	May, 1870.	October, 1869.	1863?
Analyst	Liebig.	G. L. Ulex.	Ed. Schwartz.	J. Molnar.
Potassium	0·038	0·071	0·101	0·098
Sodium	6·014	6·972	6·629	6·777
Calcium	0·373	0·445	0·369	0·315
Magnesium	3·203	4·484	3·172	3·593
Iron	0·003	0·004	0·001	0·003
Silicic acid	0·001	0·015	trace	0·004
Sulphuric acid.....	23·619	31·212	23·924	25·848
Chlorine	0·792	1·017	0·856	0·912
Combined carbonic acid	1·010	0·660	1·538	1·445

* N. Repert. Pharm., xx, 387.

The following numbers represent these compositions calculated as salts:—

Potassium sulphate	0·085	0·158	0·224	0·218
Sodium ,,	15·915	17·927	16·435	16·794
Magnesium ,,	16·016	22·422	15·858	17·967
Calcium ,,	..	1·512	..	..
Sodium chloride	1·305	1·676	1·411	1·503
,, carbonate	0 796	1·166	1·734	1·719
Calcium ,,	0·933	..	0·923	0·786
Ferric oxide and alumina	0·004	0·006	0·001	0·010
Silica	0·001	0·012	trace	0·013
Total fixed constituents	35·055	44·879	36·586	39·010
Free and semi-combined carbonic acid	0·523	..	8·253 ccs.	0·950

These numbers show that the waters approximate in character to those of Püllna, from which indeed they chiefly differ in containing all the magnesium as sulphate instead of partly as chloride.

C. R. A. W.

Analysis of Mineral Waters from the Cold Springs of the Euganian Hills in the Province of Padua. By G. Bizio.*

	Monte Ortone. New spring.	S. Daniele.	Costa di Arquà, or Acqua Raineriana.
Hydrogen sulphide	0·04642	0·01128	0·03873
Carbonic anhydride of calcic bicarbonate	0·16104	0·12458	0·16649
Calcium carbonate	0·36599	0·28314	0·37840
Calcium sulphate	0·37847	0·25821	0·03472
Sodium sulphate	0·48191	0·19365	0·16284
Sodium chloride	1·79924	1·12408	0·68491
Potassium chloride	0·11230	0·06343	0·03996
Lithium chloride	0·00062	0·00050	0·00031
Magnesium chloride	0·28141	0·17552	0·08303
Iron oxide and alumina	0·00385	0·00215	0·00137
Silica	0·03803	0·02681	0·01972
Organic matter	0·05488	0·03439	0·03880
Total fixed constituents, calculated	3·51670	2·16188	1·44406
,, ,, found	3·59860	2·21010	1·45150

The numbers express the quantity of each constituent in 1,000 parts of water.

H. W.

* Gazzetta chimica Italiana, i, 322.

Organic Chemistry.

New Contributions to the History of Carbon. By M. BERTHELOT.*

I. *Carbon of the Cranbourne Meteorite.*—This meteorite, found at Cranbourne near Melbourne, contains, among other things, fragments of pyrites and a certain quantity of amorphous carbon. The amorphous carbon was first treated with nitric acid, to remove admixed pyrites, and then with a mixture of fuming nitric acid and potassium chlorate.

By two treatments a greenish graphitic oxide was obtained, identical in all respects with the oxide from the graphite which crystallises from molten cast-iron, but different from the oxide obtained from plumbago.

From its association with pyrites in the meteorite, the carbon may have arisen from the action of carbon bisulphide on the incandescent iron, at any rate it has been formed under the influence of a very high temperature.

II. *Carbon from the Decomposition of Carbonic Oxide by Iron.*—In the decomposition of carbonic oxide by iron, and oxide of iron, at a comparatively low temperature, a large quantity of amorphous carbon is produced. By repeated treatment with nitric acid and potassium chlorate, this carbon dissolves almost completely, in the same way as the combined carbon in carburetted iron and manganese; a trace only of graphitic oxide is formed.

W. H. D.

Reactions of Carbon Bisulphide. By F. SESTINI.†

Solubility in water. Carbon bisulphide is not quite insoluble in water. After several days' contact at ordinary temperatures, water takes up about 1 pt. in 1,000 of its weight of this compound, a very small quantity at the same time undergoing decomposition. The aqueous solution when distilled gives up the carbon bisulphide unaltered, at the commencement of the distillation. It has the odour of the compound, a slightly burning taste, and does not contain more than 0·002 grm. of hydrogen sulphide in a litre.

Reactions with the Hydrates of the Alkaline earths. When a mixture of water, calcium hydrate, and carbon bisulphide is exposed to the

* Comp. rend, lxxiii, 494. † Gazzetta chimica Italiana, i, 473.

action of solar light in summer, the liquid in six or eight hours acquires a fine yellowish-red colour, and during the following night deposits a few very fine prisms of an orange-red colour.

The same reaction takes place in two hours when carbon bisulphide is heated to about 50° with milk of lime. The liquid filtered while hot does not deposit any crystals on cooling, but on adding calcium hydrate to the cooled filtrate, it yields the prismatic crystals above mentioned.

These crystals consist of a compound of hydrate and sulphocarbonate of calcium, represented by the formula $3CaH_2O_2.CaCS_3 . 7H_2O$. The formation of the sulphocarbonate, which however is preceded by that of sulphide of calcium, is represented by the equation:

$$3CaH_2O_2 + 3CS_2 = 2CaCS_3 + CaCO_3 + 3H_2O.$$

Hydrate of barium acts exactly like hydrate of calcium, and gives rise to a yellow compound which crystallises in short prisms.

The hydrates of strontium and magnesium likewise act in the same manner (the latter but feebly), but do not yield crystallised compounds.

The reaction with calcium hydrate may be applied to the detection of carbon bisulphide in solution (see *Analytical Chemistry*, p. 1090).

H. W.

On Petroleum. By H. Byasson.*

Byasson has examined the petroleum of Pennsylvania, from which he has, by numerous fractional distillations, separated fourteen liquid hydrocarbons, whose boiling points agree very closely with those of similar products obtained by Pelouze and Cahours from Canadian petroleum. The author has endeavoured to separate, by fractioning, the solid hydrocarbons known as paraffin; five solid products were separated, having the following melting-points: 30°, 41°, 50°, 58°, and 65°.

From practical difficulties in the investigation, and from the fact that these bodies alter slightly during distillation, it cannot be affirmed whether five distinct paraffins were really obtained, or mixtures of two or three.

It is pointed out that in distilling large quantities of petroleum (1,500 to 2,000 litres), the low conducting power for heat possessed by the hydrocarbons acts prejudicially in causing incomplete separation of the most volatile portions of the oil, and also partial decomposition of that part of the petroleum which is in direct contact with the source of heat, by which decomposition volatile hydrocarbons are produced.

* Compt. rend., lxxiii, 609.

In the distillations in glass retorts, bundles of very fine iron wire were employed to avoid this inconvenience, by acting as conductors; Byasson thinks that the same device could be used on the large scale.

For determining the relative inflammability of petroleums, he prefers the use of a little apparatus, by means of which the tension of the vapour of the oil at different temperatures is approximately determined by observing the height of a column of water. The most inflammable and volatile portions of the petroleum have a considerable tension, and the presence of 5 to 10 per cent. of these bodies is very dangerous.

W. H. D.

On the Petroleum of the Bas-Rhin. By Le Bel.*

In the department of the Bas-Rhin, bitumen is obtained from the mines of Schwabwiller, Pechelbronn, and Lobsann. The Schwabwiller mine is the only one which furnishes ready-formed saturated hydrocarbons boiling at a low temperature, similar to the American petroleum; the Lobsann mine yields only an almost solid bitumen.

From Pechelbronn, a black viscous product is obtained, specific gravity 0·90 to 0·97. It is principally composed of very dense oils (0·89 to 0·94), not acted on by sulphuric acid; the most volatile constituent is petrolene, described by Boussingault. Besides these, there have been isolated: paraffin, a colourless and solid resin, and a black substance containing oxygen.

On distillation, the crude products yield carbon and volatile oils; the portion distilling below 70° was separated into two parts: one distilling between 60° and 70°, the other between 30° and 40°. Amyl hydride can be extracted from the products which distil at 30°—40°, hexyl hydride from the 60°—70° fraction. The liquid which boiled below 70° contained also amylene; the hydriodide was obtained by heating the hydrocarbons with fuming hydriodic acid; it boiled at 143°—146°. Its boiling point is that of the hydriodate of ethyl-allyl; moreover the hydriodide of amylene from the petroleum requires the assistance of heat for complete action on silver oxide or acetate, which is not the case with ordinary hydriodide of amylene. The action of silver acetate furnished isoamyl acetate, and from this an alcohol boiling at 113°—121° was obtained, which did not yield a sulpho-acid with sulphuric acid. Ethyl-allylic alcohol, according to Wurtz, boils at 120°.

W. H. D.

The Influence of Sunlight on Petroleum Oils. By M. Grotowsky.†

In some recent experiments the author has shown, that when petroleum oils are exposed, under certain conditions, to sunlight, they absorb oxygen from the air, which is converted into ozone, a pheno-

* Compt. rend., lxxiii, 499. † Pharm., J. Trans. [2], ii, 226.

menon that has already been observed in some other hydrocarbons. No chemical combination takes place between the oil and the ozone, but the latter remains free, and oxidises strongly any substance with which it comes in contact.

In oils containing ozone the smell is completely modified; they burn with difficulty, and attack rapidly the stoppers of the vessels containing them, especially if the stoppers be of cork. When glass vessels are used, it has been found that the colour of the glass exercises a great influence over the absorption of oxygen. Decolorised oils, exposed in white glass vessels to the action of sunlight, turn yellow, become charged strongly with ozone, and burn with difficulty. This is principally the case with the American petroleums. They should, therefore, be kept in metallic vessels, or, if glass be used, it should be shaded as much as possible from the sun.

On Quintanes. By M. Lwow.*

On adding zinc-methyl, drop by drop, to methyl-chloracetol, $CH_3 - CCl_2 - CH_3$, no reaction sets in before equal molecules are present, but it then becomes very violent, and always ends with an explosion. But when methyl-chloracetol is gradually added to zinc-methyl, a quiet reaction sets in on gently heating, and then goes on without further application of heat. The gas given off has all the properties of *tetra-methyl-methane*, $C(CH_3)_4$; but it does not crystallise at $-30°$, whilst that which the author previously obtained solidified at $-20°$. Probably the gas contained traces of impurities.

To obtain the normal quintane†, normal butyl iodide and zinc-methyl were heated together in different proportion, without any action taking place, whilst tertiary butyl iodide is very easily acted upon by zinc-methyl. By heating the normal iodide with methyl iodide and zinc, only zinc-methyl is formed, and by acting in the same way upon the tertiary iodide, reaction sets in in the cold, the product being a gas and a high-boiling liquid, probably consisting of polybutylenes. By adding sodium to a solution of the normal iodide and methyl iodide, the iodide is not acted upon, either in the cold or on boiling.

Methylene iodide and zinc-ethyl act easily on each other, the following reaction taking place:—

$$2Zn(C_2H_5)_2 + 2CH_2I_2 = (C_2H_5)_2 + C_2H_4 + 2ZnI_2.$$

C. S.

* Zeitschr. f. Chem., xiv, 257—258.

† Normal quintane exists in considerable quantities in the volatile portions of Pennsylvanian petroleum, and of Cannel and Boghead tar. It boils at 38°, and can easily be converted into a primary and a secondary alcohol, the former yielding on oxidation Lieben's normal valeric acid, and the latter methyl-propyl ketone.—C. S.

On the Preparation of Methylene Iodide. By J. BLJUDUCHO.*

LIEBEN obtained this compound by the action of hydriodic acid upon chloroform. On mixing these compounds in the proportion indicated by the equation—

$$CHCl_3 + 4HI = CH_2I_2 + 3HCl + I_2,$$

5 grams of chloroform yielded 9 grams of methylene iodide, the theoretical yield being 11·21 grams from 5 grams of chloroform.

On preparing it according to the equation—

$$CHCl_3 + 3KI + HI = CH_2I_2 + 3KCl + I_2,$$

only 3·3 grams were formed, but by using only half the quantity of hydriodic acid, 7 grams were obtained.

C. S.

Communications from the Chemical Laboratory of the University of Kasan.†

On the Structure of Propylene Chloriodide. By W. SOROKIN.—On heating propylene chloriodide, C_3H_6ClI, with an alcoholic potash-solution, monochloropropylene is formed, and not, as Simpson states, the isomeric compound, allyl chloride. From this it follows that the structure of propylene chloriodide is $CH_3.CHCl.CH_2I$.

Allylene hydriodide, $C_3H_4.2HI$, has the structure $CH_3—CI_2—CH_3$, as by the action of moist oxide of silver it is converted into acetone.

On the Structure of Ethylene. By W. KRIWASIN.—On oxidising ethylene chlorhydrin with a dilute solution of potassium dichromate and sulphuric acid, monochlor-acetic acid is obtained, showing that the chlorhydrin has the structure $CH_2Cl - CH_2OH$.

On the so-called Dichloracetone. By the same.—The author could not obtain this compound, which was prepared by Fittig and Borshe by the action of chlorine on acetone; he obtained only a complicated mixture containing monochloracetone and products of higher-boiling point, apparently a mixture of condensation-products of acetone and monochloracetone.

On the Decomposition of Ethylene Bromide by Water. By the same. —On heating these substances together to 150—160°, Carius obtained hydrobromic acid and aldehyde. The author obtained no aldehyde whatever, and only a doubtful trace of a condensed aldehyde. He believes that Carius's aldehyde ammonia was nothing but ammonium bromide.

On the Hydrocarbon, C_7H_{14}, *and its Derivatives.* By W. MARKOWNI-

* Zeitschr. f. Chem. xiv, 258. † Zeitchr. f. Chem. [2], vii, 263—269.

KOW.—This hydrocarbon is formed by heating oxy-isocaprylic acid, $(C_3H_7)_2C(OH)CO_2H$, with water and a few drops of sulphuric acid to 180°. The pure hydrocarbon is a colourless mobile liquid, having the odour of the volatile olefines and boiling at 81°—83°. It is formed by the reaction—

$$C_8H_{16}O_3 = C_7H_{14} + CO_2 + H_2O,$$

a decomposition which has hitherto been observed only amongst the aromatic acids. This pseudoheptylene combines with bromine and with hydriodic and hydrobromic acids.

By decomposing the pseudoheptyl iodide, $C_7H_{14}HI$, with freshly-precipitated silver oxide, pseudoheptyl alcohol is formed, a light, oily liquid, boiling at about 130° and smelling like camphor. It is a tertiary alcohol which, on oxidation, yields no acetone, but fatty acids containing less carbon in the molecule. The structure of pseudoheptylene is probably $(CH_3)_2.C.CH.CH.(CH_3)_2$.

On the Oxidation-products of Dichlorhydrin. By the same.—On oxidising this compound, which was obtained from epichlorhydrin, dichlor-acetone was formed, showing that this chlorhydrin has the structure $CH_2Cl.CHOH.CH_2Cl$.

In working with epichlorhydrin or dichloracetone, care has to be taken not to bring them on the finger, as in this case, after a few hours convulsions set in, and quickly extend over all the fingers, which soon begin to swell. These symptoms do not disappear completely for some months.

C. S.

On Benzene Hexchloride. By ZACHAR HEYS.*

PURE benzene hexchloride is readily obtained by acting on boiling benzene with excess of chlorine, evaporation of unaltered benzene, and recrystallisation from benzene or alcohol of the crystals that separate on cooling, after freeing them from mother-liquor by pressure; it melts at 157° (Mitscherlich states its melting point at 132°, Laurent at 135°—140°). Treated with alcoholic potash it furnishes pure trichlorobenzene, boiling constantly at 207°, fluid at ordinary temperatures, but becoming a crystalline solid at temperatures below 0°. According to Vohl† fuming nitric acid yields with the hexchloride a crystalline compound; the writer says this statement is erroneous, neither boiling with fuming nitric acid for many hours, nor treatment with a hot mixture of nitric and sulphuric acids having any action on it: hence the formation of nitro-compounds in the aromatic series does not depend on the ring-form of benzene, but on the fact of its consti-

* Zeitschr. f. Chem. [2], vii, 293. † Zeitschr. f. Chem. [2], iii, 122.

tuent carbon atoms being doubly united; possibly, however, the chlorine atoms may influence the adjacent hydrogen, and prevent their substitution by NO_2.

When the hexchloride is heated to 150° with alcoholic potassium acetate, much potassium chloride is formed; on cooling, the filtrate deposits colourless crystals, insoluble in water, sparingly soluble in cold alcohol, but readily dissolved by boiling alcohol; these crystals melt at 250°. Simultaneously a fluid compound is produced, probably trichlorobenzene.

C. R. A. W.

On the Action of Sodium on Bromotoluene. By RUDOLPH FITTIG.*

THE author has formerly shown that the action of sodium on fluid bromotoluene, purified by distillation only, gives rise to a fluid hydrocarbon, *ditolyl*, and a solid crystalline body, which, from its melting point, physical characters, and composition, he considered to be identical with stilbene. Zincke and Louguinine, who have recently examined this same reaction with *pure* para-bromotoluene, have likewise formed both a liquid and a solid product, but Zincke concludes from his experiments that the latter is not stilbene, but an isomeride of ditolyl. Fittig has repeated his observations on the solid hydrocarbon formerly obtained by him, and concludes that Zincke is correct, inasmuch as the analytical numbers agree better with those required for the formula of ditolyl than of stilbene, and no stilbene bromide is obtainable by treatment of its ethereal solution with bromine, although a compound is obtainable, the examination of which he postpones until the conclusion of Zincke's labours on ditolyl.

C. R. A. W.

Observations on the Simultaneous Distillation of Water and Certain Alcohols Insoluble in Water. By IS. PIERRE and ED. PUCHOT.†

WHEN a mixture of amylic alcohol and water is submitted to distillation, ebullition commences at 96 , and remains remarkably constant at this point. The authors find that so long as these temperatures remain constant, the volumes of water and of amylic alcohol condensed during any given time are invariably in a constant ratio, viz., 2 to 3, and that the temperature does not begin to rise until either the water or the alcohol has wholly distilled over, leaving a surplus of alcohol or of water (as the case may be) in the retort. If the water was originally more than two-thirds of the volume of the alcohol, the temperature rises to 100° as soon as the whole of the alcohol has distilled over; but if less than the two-thirds of water was originally present, the

* Zeitschr. f. Chem. [2], vii, 298. † Comptes rendus, lxxiii, 599.

boiling point rises to 130° as soon as the whole of the water has distilled over, amylic alcohol only being then left.

Butylic alcohol gives precisely analogous results, the volumetric ratio in this case being 1 of water to 5 of alcohol; the boiling point of the mixture is perfectly constant at 90·5°, *i.e.*, 9·5°, below the boiling point of water, and 17·5° below that of butylic alcohol; fourteen experiments gave absolutely the same numbers in each instance.

When a mixture of water, butylic, and amylic alcohols is used, the temperature of ebullition is not constant, but regularly rises; the temperature, however, always lies between 90·5° and 96°, being higher the larger the proportion of amylic alcohol present; the relative volume of water that distils over also continually increases, being, however, always greater than $\frac{1}{6}$th of the total volume that passes over, and less than $\frac{2}{5}$ths; *i.e.*, lying between the relative numbers found with butylic alcohol and water, and with amylic alcohol and water.

C. R. A. W.

Synthesis of Normal Propyl Alcohol from Ethyl Alcohol. By A. Rossi.*

1. *Preparation of Propionic Aldehyde*, $C_3H_6O = C_2H_5,CHO$.—Propionic acid, prepared by heating ethyl cyanide with pulverised potash in an apparatus with reversed condenser, as long as ammonia is given off, and decomposing the resulting potassium salt with dilute sulphuric acid, is converted into a calcium salt; and an intimate mixture of this salt with an equal weight of calcium formate, dried at 100°, is subjected to distillation by small portions at a time (10 to 12 grams) in a retort uniformly heated over a charcoal fire, and connected with a receiver cooled by a freezing mixture. A yellowish liquid then distils over, having a very pungent odour of aldehyde, and distilling for the most part below 70°; and by subjecting this portion to repeated fractional distillation, a liquid is at length obtained, boiling between 40° and 50°, and amounting to about a fourth of the crude product. This liquid consists of propionic aldehyde, contaminated with a small quantity of water, which may be removed by agitation with calcium chloride. The remaining three-fourths of the distillate consists partly of a liquid boiling at 60°—80°, and combining with alkaline bisulphites, probably butylic aldehyde, partly of another liquid boiling at 80° and not uniting with alkaline bisulphites.

Propionic aldehyde, purified as above, is a very limpid, colourless liquid, more mobile than water, having a very sharp and suffocating aldehydic odour, and soluble in rather more than three times its own weight of water. It boils at 40°—45° under a pressure of 0·740 met.,

* Gazzetta chimica Italiana, i, 230—239.

and has a specific gravity of 0·8047 at 0°. The analysis gave 62·20 p. c. C., and 10·32 H.; calc. 62·05 C., and 10·34 H. It oxidises in the air, and quickly reduces ammoniacal silver nitrate, producing a speculum of silver. It dissolves with great rise of temperature in $1\frac{1}{2}$ vol. of a concentrated solution of sodium bisulphite, forming a compound which crystallises on cooling. The solution distilled with potassium carbonate reproduces the aldehyde, mixed with a liquid of higher boiling point, probably resulting from an alteration of the aldehyde by the action of the alkaline carbonate.

2. *Normal Propyl Alcohol*, $C_3H_8O = CH_2CH_3 . CH_2OH$.—This alcohol is obtained by the action of nascent hydrogen on propionic aldehyde. The aldehyde in small portions (10 to 12 grams) dissolved in about 12 times its weight of water, is introduced into a flask standing in iced water, and sodium-amalgam, containing about 1 p. c. sodium, is introduced in portions of 100 grams at intervals of an hour, together with a quantity of sulphuric acid, sufficient to render the liquid slightly acid. As the sodium-sulphate produced in the reaction causes the propionic aldehyde to separate from the solution, and thereby interferes with the action of the hydrogen, it is best, after having added from 700 to 800 grams of the amalgam, to distil the product, and subject the distillate to renewed treatment with sodium-amalgam till the liquid no longer sensibly reduces ammoniacal silver-nitrate, which will be the case after three or four additions of the amalgam. The products of the several operations are then collected; the whole is filtered to separate an oily substance; the filtered liquid is repeatedly distilled, collecting always the first portions of the distillate which contain the largest proportion of propylic alcohol; and the entire distillate is treated with pulverised potassium-carbonate, to liberate the propylic alcohol which then floats on the surface like an oil, and is easily separated by decantation. The quantity of crude and moist propylic alcohol thus obtained amounts to about $\frac{7}{10}$ths of the propionic aldehyde used. It is purified by treatment with potassium carbonates and repeated fractional distillation, and freed from the last portions of water, which it retains with obstinacy, by distilling it several times over sodium.

Propyl alcohol thus prepared is a very limpid, colourless liquid, more mobile than water, having a strong but not unpleasant odour, much like that of common alcohol. It dissolves in all proportions of water, boils at about 96° under a pressure of 0·745 met., and has a specific gravity of 0·8205 at 0°. Analysis 59·94 p. c. C., and 13·44 H., calc. 60·00 C., and 13·33 H.

Propyl alcohol treated with sodium rapidly evolves hydrogen, and forms a very white crystalline mass, which may be heated considerably above 100° without turning brown, and reproduces the alcohol when

distilled. The aqueous solution of the alcohol, gently heated with iodine and potash, yields iodoform. By oxidation with potassium dichromate and sulphuric acid, it yields, as sole product, propionic acid.

3. *Propyl Bromide*, $C_3H_7Br = CH_2CH_3 . CH_2Br$, is prepared by saturating the alcohol cooled by ice with gaseous hydrogen bromide, of which it absorbs about an equal weight, and heating the resulting solution with an equal volume of strong aqueous hydrobromic acid, first to 70°, and then gradually to 105°, till the proportion of the two layers into which the liquid divides itself becomes constant. The ethereal layer, separated and purified in the usual way, yields propyl bromide as a very limpid colourless liquid, having an ethereal odour, not altered by light, boiling at 70°—71° under a pressure of 0·749 met., and having a specific gravity of 1·3887 at 0°.

4. *Propyl Iodide*, $C_3H_7I = CH_2CH_3 . CH_3I$, is prepared by treating propyl alcohol with iodine and amorphous phosphorus in a vessel standing in cold water, distilling after 12 hours, then washing with alkaline water, drying with calcium-chloride, and rectifying.

When recently prepared it is a colourless liquid, but gradually acquires a brownish yellow colour, especially if exposed to light. It smells like ethyl iodide, boils at 102° under a pressure of 0·752 met., and has a specific gravity of 1·7821 at 0°.

5. *Propyl Acetate*, $C_3H_7 . C_2H_3O_2 = CH_2CH_3 . CH_2(OC_2H_3O)$, prepared by heating the iodide with a slight excess of silver acetate, moistened with glacial acetic acid, is a colourless liquid having a very fragrant fruity odour, nearly insoluble in water, boiling at 100°—101° under a pressure of 0·750 met., and having a specific gravity of 0·913 at 0°. Heated in sealed tubes with strong potash-ley it reproduces the alcohol.

6. *Propyl Cyanide*, $C_4H_7N = CH_2CH_3 . CH_2CN$, prepared by heating the bromide or iodide to 105° in sealed tubes with pulverised potassium cyanide dissolved in alcohol of 85 p. c., is a liquid having a very pungent disagreeable odour. By heating it with alcoholic potash in an apparatus with reversed condenser as long as ammonia continues to escape, a potassium salt is obtained, which, when distilled with dilute sulphuric acid, yields normal butyric acid, $C_4H_8O_2 = CH_2CH_2CH_3 . COOH$, as a limpid colourless liquid, having a pungent odour of acetic acid and of cheese, soluble in all proportions of water, boiling at 163° under a pressure of 0·742 met., and having a sp. gr. of 0·977 at 0°.

The calcium salt of the acid thus obtained crystallises in perfectly white laminæ, unctuous to the touch, having a faint odour of cheese, moderately soluble in water, and forming a solution which becomes turbid when slightly heated, and yields an abundant crystal-

line deposit. These characters are exactly those of the butyric acid of fermentation, whence it follows that this acid has the constitution of normal butyric acid, and is the true homologue of acetic acid.

From the facts above detailed it appears that propionic aldehyde is formed—contrary to the statement of Siersch*—by distilling a mixture of propionate and formate of calcium; and that this aldehyde, by fixing 2 atoms of hydrogen, is converted into normal propyl alcohol. Hence, and from the synthesis of normal butylic and amylic alcohols recently effected by Lieben and Rossi, it may be inferred that this mode of synthetic formation of the normal alcohols $C_nH_{2n+2}O$ is perfectly general.

H. W.

Normal Amyl Alcohol and Normal Caproic Acid. By A. Lieben and A. Rossi.†

The calcium salt of normal valeric acid (p. 1045) distilled with calcium formate, yields normal valeric aldehyde, $C_5H_{10}O$, which boils at 102°, and may be separated by fractional distillation from the less volatile pyrogenic substances by which it is accompanied. It is but slightly soluble in water, smells like ordinary valeral, and unites with alkaline bisulphites.

To transform this aldehyde into normal amyl alcohol, it is mixed with 30 parts of water (not sufficient to dissolve it completely), and heated with sodium amalgam and sulphuric acid, in the manner already described for the preparation of normal butyl and propyl alcohols (pp. 517, 1032). The crude alcohol thus obtained is dried with calcium chloride and purified by fractional distillation, and finally by digestion and distillation over lime, baryta, and sodium in succession. The alcohol thus purified, gave by analysis 68·42 p. c. C. and 13·88 H., the formula $C_5H_{12}O$ requiring 68·18 C., and 13·64 H.

Normal Amyl Alcohol is a colourless liquid smelling like the amyl alcohol of fermentation. It boils at 137° (about 8° higher than ordinary amyl alcohol). Its specific gravity at various temperatures is given in the following table:—

Temperature	0°	20°	40°	99·15°
Specific gravity ..	0·8296	0·8168	0·8065	0·7835

By oxidation with chromic acid mixture, it is converted into valeric acid.

Normal Amylic Ethers. The *chloride*, $C_5H_{11}Cl$, boils at 106° under a pressure of 0·7398 met. (the thermometer completely immersed in the

* Ann. Ch. Pharm. cxlii, 115. † Gazzetta chimica Italiana, i, 314—322.

vapour); and has a density of 0·9013 at 0°, 0·8834 at 20°, 0·868 at 40°. The *bromide*, $C_5H_{11}Br$., boils at 128·7° (bar. at 0·7394), and has a density of 1·246 at 0°, 1·2234 at 20°, 1·2044 at 40°. The *iodide*, $C_5H_{11}I$, boils at 155·4 (bar. at 0·7393 met.), and has a density of 1·5435 at 0°, 1·5174 at 20°, 1·4961 at 40°. The *acetate*, $C_5H_{11},C_2H_3O_2$, boils at 148·4° (bar. at 0·737 met.), and has a density of 0·8963 at 0°, 0·8792 at 20°, 0·8645 at 40°.

Normal Caproic Acid, $C_6H_{12}O_2 = C_5H_{11}.COOH$. Amyl cyanide prepared from the bromide or iodide by a process similar to that already described for propyl cyanide (p. 1033), was converted into caproic acid by heating it with alcoholic potash, and decomposing the resulting potassium salt with sulphuric acid. The acid then separates as an oily layer, which may be purified by washing and distillation.

Normal caproic acid is a colourless liquid which does not mix with water, has an odour fainter and somewhat less disagreeable than that of ordinary caproic acid, and a strongly acid taste. It boils at 204·5°—205° (bar. at 0·7385 met.), ordinary caproic acid boils at 199·7°. Its specific gravity at different temperatures is as follows:—

Temperature	0°	20°	40°	99·1°
Specific gravity ..	0·9449	0·9294	0·9172	0·8947

We are now acquainted with five amylic alcohols, the constitution of which is represented by the following formulæ:—

Primary.		Secondary.		Tertiary.
CH_3	H_3C CH_3	CH_3	H_3C CH_3	CH_3
CH_2	\ /	CH_2	\ /	H_2C CH_3
CH_2	CH	CH_2	CH	\ /
CH_2	CH_2	CHOH	CHOH	COH
CH_2OH	CH_2OH	CH_3	CH_3	CH_3
Normal amyl alcohol.	Inactive amyl, alcohol of fermentation.	Propyl-methyl carbinol, or hydrate of ethyl-allyl.	Isopropyl-methyl carbinol, or hydrate of amylene.	Ethyl-dimethyl carbinol.
B. P. 137°.	128—132°.	120—123°.	104—108°.	98·5—100°.

The boiling points of these alcohols (like those of the isomeric butyl alcohols) go on increasing from the tertiary to the normal primary. To complete the series of the five carbon alcohols, there are still three wanting, two primary and one secondary.

The constitution of normal amyl alcohol is established by the mode of its formation; that of the inactive fermentation alcohol is deduced from that of the corresponding valeric acid, established by Erlenmeyer

and by Frankland and Duppa. The active fermentation alcohol differs from the ordinary inactive modification only in its action on polarised light, and it is at present uncertain whether this modification has the constitution of one of the missing primary amyl alcohols, or whether the active and inactive alcohols are merely physically isomeric. According to Schorlemmer, the amyl alcohol prepared from quintane, C_5H_{12} (from American petroleum), is identical with ordinary amyl alcohol.

The constitution of normal caproic acid is shown, by its formation from normal amyl alcohol, to be $CH_3CH_2CH_2CH_2CH_2.COOH$.

H. W.

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*Communications from Butlerow's Laboratory.**

I. *On the Properties of Trimethyl-carbinol.*—By A. Butlerow. Perfectly dehydrated trimethyl-carbinol forms long, rhombic, doubly-refracting needles or tables, which melt at 25°—25·5°, and very readily attract water, becoming liquid. It boils at 82·5°, under a pressure of 750 mm.; its specific gravity at + 30 = 0·7788; its co-efficient of expansion between + 30 and + 50 is 0·0136 for 1°. On adding water to trimethyl-carbinol, considerable contraction takes place. The hydrate of trimethylcarbinol, $2C(CH_3)_3.OH + H_2O$, is liquid at 0°, and boils constantly at 80°. In a mixture of snow and salt it crystallises in fine, silky needles.

II. *Triethyl-carbinol.* By A. Nahapetian.—The triethyl-carbinol was prepared from propionic chloride and zinc-ethyl. A mixture of the two substances, in the proportion of 1 mol. acid chloride to 2 mols. zinc ethyl, was allowed to stand for some days, and then heated to 100°. Water was added, the alcohol dissolved in a sufficient quantity of water, and the solution filtered from insoluble oil. The alcohol, separated from the aqueous solution by potassium carbonate, was dried by baryta and repeatedly rectified.

Triethyl-carbinol $C(C_2H_5)_3OH$ is liquid, even at − 20°, boils at 140°—142°, is but slightly soluble in water, and has a specific gravity = 0·8593 at 0°. Oxidised by a mixture of three parts potassium bichromate, 1 part oil of vitriol, and 4 parts water, the alcohol gave besides some carbon dioxide, a heptylene represented by the formula $(C_2H_5)_2{=}C{=}CH - CH_3$. The ketone, $CO(C_2H_5)_2$, was not observed, but acetic and propionic acids appear to have been produced.

III. *Dimethylpseudopropyl-carbinol.* By J. Prianicknikow.—This alcohol, $C.OH.(CH(CH_2)_2).CH_3.CH_3$, is produced from isobutyryl chloride, $CO.Cl.(CH(CH_3)_2)$, and zinc-methyl. The isobutyryl chloride was prepared from the butyric acid resulting from the oxidation of fermentation butyl alcohol by chromic acid. The chloride was gradually added to the zinc methyl, in the proportion of 1 mol. of the former to

* Zeitschr. f. Chem. [2], vii, 273–275.

2 mols. of the latter; the mixture was left to itself for a week, and the resulting crystalline mass decomposed by water, the alcohol distilled off, and dried by baryta.

The alcohol is liquid at the ordinary temperature, but becomes solid at $-35°$; it boils at 112°—113°, is soluble in water, and has a specific gravity = 0·8364 at 0°. By boiling it for an hour with the above-mentioned oxidising mixture, acetone and a little acetic acid are produced: $C_6H_{14}O + O_2 = 2C_3H_6O + H_2O$.

IV. *On a New Amylene.* By M. Ermolaien.—Dimethylethyl-carbinol, prepared from propionic chloride and zinc-methyl, yields an iodide when treated with hydriodic acid gas. This iodide is decomposed by very concentrated alcoholic potash without external heating, a liquid, $C_5H_{10} = C(CH.CH_3).CH_3.CH_3$ or $C.CH_2.CH_3.(CH_2.CH_3)$, being produced. This amylene boils at 35°, unites with bromine, and with fuming hydriodic acid when heated to 100°, with formation of the original iodide; this iodide is converted into dimethylethyl-carbinol by treatment with silver oxide and water.

W. H. D.

On Nitro-ethal, Nitro-glycol, and a general Method of Transforming Alcohols into their corresponding Nitric Ethers. By P. Champion.*

Powdered ethal is added little by little to a mixture of sulphuric and nitric acids; no appreciable amount of heat is evolved, but after agitation the ethal becomes transformed into a milky substance, which is decanted and freed from admixed acids by solution in ether, and agitation of the ethereal liquid with water; finally the ether is evaporated, and ultimately leaves *nitroethal* as an oily liquid, which is practically colourless if pure ethal has been used. Thus obtained nitroethal is soluble in ether, carbon disulphide, and chloroform; ethylic and methylic alcohols dissolve it but sparingly; on a strongly-heated plate it becomes spheroïdal, and burns with a smoky flame; by heating alone it is decomposed, leaving a coaly residue; it solidifies between 10° and 12°, and has the specific gravity 0·91; strong sulphuric acid decomposes it; by analysis it was found to have the formula $C_{16}H_{33}(NO_2)O$.

Nitroglycol is similarly obtainable by using a mixture of 100 parts fuming nitric acid, 200 of concentrated sulphuric acid, and 42 of glycol, and observing the directions formerly described in the preparation of nitroglycerin. Nitroglycerin (*sic* (?) nitroglycol) is a colourless, mobile liquid of a sweet taste, and poisonous; its specific gravity is 1·48; though but little volatile at common temperatures, it is markedly so at 100°; it is soluble in ether and alcohol, but insoluble

* Comptes rendus, lxxiii, 571.

in water; kept at $-15°$ for two hours it did not crystallise; percussion detonates it, but it does not explode when heated on a plate; thus heated, it volatilises at 185°, and more abundantly at 230°, giving off yellow vapours; at 295° it becomes spheroïdal. Its vapour, according to Dr. G. Birgeron, produces, when inhaled, sleepiness and intense and continuous pains in the head; $\frac{1}{2}$ c.c. injected under the skin of a rat, produced in about an hour somnolence and vertigo; the animal then fell into a comatose state, and finally died: six or eight drops under a belljar produced the same symptoms in a bird.

The author considers that the action of mixed sulphuric and nitric acids on alcohols is a general method for procuring nitric ethers, a low temperature being occasionally indispensable; thus ethyl nitrate and amyl nitrate require the materials to be cooled to $-15°$; by this means octyl nitrate has been obtained identical (?) with that which Bouis obtained by the action of octyl iodide on silver nitrate. In the same way many new chloro- and bromo-nitrated compounds may be formed.

C. R. A. W.

On the Reduction Products of Silicic Ether and some of their Derivatives. By A. Ladenburg.*

Friedel and Ladenburg,† when preparing silicopropionic ether by the action of zinc-ethyl and sodium on $SiCl(OC_2H_5)_3$, noticed the simultaneous formation of a body containing more carbon and hydrogen than the above ether; this they held to be probably $Si(C_2H_5)_2(OC_2H_5)_2$. It might have been formed by the reduction of silicopropionic ether, $SiC_2H_5(OC_2H_5)_3$. In order to test the correctness of this hypothesis and to obtain the still unknown reduction-products, $Si(C_2H_5)_2(OC_2H_5)_2$ and $Si(C_2H_5)_3OC_2H_5$, the author has studied the action of zinc-ethyl and sodium on silicic ether.

Reaction soon takes place on warming, and is accompanied by a slight evolution of gas; the sodium becomes covered with a crust of zinc, and a black mass is deposited at the bottom of the vessel also consisting partially of zinc. The action gradually diminishes until finally, even at the boiling point of the mixture, no further change takes place. The product obtained on distillation was always contaminated by zinc-ethyl, which was removed by fractioning. The composition and properties of the substances obtained vary according to the amount of zinc-ethyl employed, but it was found advisable first to allow reaction to take place between equal molecules of ether and zinc-ethyl, and to subject the product anew to the action of the latter and sodium.

* Deut. Chem. Ges. Ber., iv, 726.

† Ibid., iii, 15; and Compt. rend., lxvi, 816.

Silicopropionic ether is the first product of the reduction of silicic ether, and was obtained with all the characteristic properties already described by the author and Friedel.

Siliciumdiethylketonic ether, $Si(C_2H_5)_2(OC_2H_5)_2$. It is necessary to subject silicopropionic ether to repeated treatment with zinc-ethyl and sodium before this body can be isolated. It boils at 155·5°, is insoluble in water, but soluble in ether and alcohol; it is distinguished from silicopropionic ether by being unattacked by alcoholic ammonia, and by the fact that concentrated sulphuric acid does not separate silicopropionic acid from it; otherwise, in appearance and smell, it is very similar to both silicic and silicopropionic ethers. It is also decomposed by a very concentrated potash-solution with much greater difficulty than silicopropionic ether, disappearing entirely only after long boiling. A vapour-density determination by Hofmann's method in paratoluidine-vapour, gave 179 as its molecular weight, as against 176 calculated.

On heating with acetyl or benzoyl chloride,* the ethoxyl groups become replaced by chlorine, with simultaneous formation of acetic or benzoic ether:—

$$Si(C_2H_5)_2(OC_2H_5)_2 + C_2H_3OCl = Si(C_2H_5)_2ClOC_2H_5 + CH_3COOC_2H_5.$$

$$Si(C_2H_5)_2(OC_2H_5)_2 + 2C_7H_5OCl = Si(C_2H_5)_2Cl_2 + 2C_6H_5COOC_2H_5.$$

The reaction is effected in sealed tubes at 200°.

Siliciumdiethylchlorethin, $Si(C_2H_5)_2ClOC_2H_5$, boils at 148°; *siliciumdiethylchloride*, $Si(C_2H_5)_2Cl_2$, at 129°. Both are fuming liquids of an odour recalling that of silicium chloride, and are decomposed by both water and alcohol, but without evolution of any considerable amount of heat. The chlorine may be replaced by acetoxyl, by warming them with acetic acid dissolved in its anhydride. The bodies formed have not yet been investigated.

The product of the decomposition of siliciumdiethylchloride by water is a viscous, almost odourless syrup, not solid even at − 15°; its boiling point seems to lie far above that of mercury. The analytical numbers correspond only roughly with the formula $Si(C_2H_5)_2O$. The same body, together with ethyl iodide, was obtained by heating siliciumdiethylketonic ether with hydriodic acid boiling at 127°; this also did not give any sharp results on analysis, and further purification of such a substance seemed hopeless. The author holds this

* The author has vainly attempted to decompose oxalic ether by acetyl chloride; Dr. Rosenthal finds that orthoformic ether is decomposed when heated therewith to 180°, according to the equation:

$$CH(OC_2H_5)_3 + C_2H_3OCl = HCOOC_2H_5 + C_2H_5Cl + CH_3COOC_2H_5.$$

compound to be identical with the product which Friedel and Crafts* obtained, by oxidising silicium-ethyl with fuming nitric acid. He proposes for it the name *silicium-diethylketone*. When heated with concentrated potash, it is attacked only after a long time, and silicopropionic acid may then be obtained from the alkaline solution. At the same time traces of a volatile acid are formed, so that the reaction is probably :—

$$Si(C_2H_5)_2O + O_3 = SiC_2H_5O_2H + C_2H_4O_2.$$

corresponding to the oxidation of diethylketone :—

$$C(C_2H_5)_2O + O_3 = C_3H_5O_2H + C_2H_4O_2.$$

Silicoheptyl ether, $Si(C_2H_5)_3OC_2H_5$. This body is obtained, though with considerable difficulty, by the prolonged action of zinc-ethyl and sodium. It boils at 153°. It is distinguished from silicium-ethyl by its behaviour with dilute hydriodic and concentrated sulphuric acids. Silicium-ethyl is neither attacked nor dissolved by these reagents, whereas silicoheptyl ether is dissolved by sulphuric acid with slight evolution of temperature, the solution depositing an oil on subsequent addition of water. On the addition of hydriodic acid, it becomes slightly warm, and at a higher temperature a somewhat energetic reaction takes place, according to the equation :—

$$2Si(C_2H_5)_3OC_2H_5 + 2HI = [(Si(C_2H_5)_3)]_2O + 2C_2H_5I + H_2O.$$

The boiling point of the siliciumtriethyl oxide thus obtained was found to be 224°—229°, or slightly lower than previously stated† (230°—235°). In the following tabular arrangement, the author calls attention to a certain regularity in the physical properties of the best known members of the silicium-ethyl series :—

	B. P.	Sp. gr. at 0°.
Silicic ether	166·5	·9676
Silicopropionic ether	158·5	·9207
Siliciumdiethylketonic ether ..	155·5	·8752
Silicoheptyl ether	153·0	·8414
Siliciumethyl.....	152·5	·7657

H. E. A.

On the Conversion of Allyl Alcohol into Acrylic Acid. By B. Tollens.‡

On oxidising the dibromide of allyl alcohol with chromic acid or nitric acid, the acid $C_3H_4Br_2O_2$ is formed, a crystalline body, which melts at

* Ann. Chim. Phys., [4], xix, 334. † Ann. Ch. Pharm., cxlvii, 255.
‡ Zeitschr. f. Chem., xiv, 305—306.

65°—66·5° and appears to be identical with Friedel's dibromo-propionic acid.

This acid reacts violently on zinc-dust, acrylic acid being formed, which was identified by its characteristic lead-salt. As the brominated acid undoubtedly contains the carboxyl group, this group must also be present in acrylic acid, and we have thus a further proof that the latter has the constitution $CH_2{=}CH - CO_2H$.

C. S.

Researches on Phenylic Ethers. By E. LIPPMANN.*

1. *Epioxyphenylhydrin.* When epichlorhydrin is heated with potassium phenate in alcoholic solution (absolute), there is formed, besides potassium chloride, an oil which separates with water, and after heating to 200° solidifies, and may be purified by pressure and by recrystallisation from alcohol. It forms prismatic crystals which have the composition $CH_2(C_6H_5O)(CH.O.CH_2)$.

2. *Action of Bromine on Potassium Phenetolsulphonate.* Bromine is added to a watery solution of potassium phenetolsulphonate until the colour ceases to be removed, when crystals mixed with oil are formed. The crystals may be purified by treatment with ether, which removes the oil, or by recrystallisation from water, when they are obtained in long needles. They are found to be the potassium salt of bromophenetolsulphuric acid, $C_6H_3Br(OC_2H_5)(SO_3K)$. By double decomposition various other salts may be obtained.

The silver salt crystallises in small brilliant plates soluble in hot water. The lead-salt in plates more difficultly soluble than the former; the barium salt in scales, and the potassium salt in needles, which lose water of crystallisation at 160°.

Bromophenetolsulphuric acid, $C_6H_3Br(OC_2H_5)SO_3H + 4H_2O$, is obtained by decomposing a solution of the potassium salt mixed with ether by sulphuric acid, as an oily layer which, on evaporation, crystallises. It is insoluble in alcohol and ether.

The oil which is formed by the action of bromine on potassium phenetolsulphate is obtained by evaporation of its ethereal solution, in prismatic tabular crystals, having the composition $C_6H_3Br_2(O.C_2H_5)$, or dibromophenetol.

3. *Monobromophenetol.* The direct bromination of phenetol gave very poor results, as the action is very violent. A better process is to decompose the potassium bromophenate with ethylic iodide at 170°; after treatment with water and fractional distillation, monobromophenetol is obtained as a liquid boiling at 233°. It is not possible to obtain an ethylated compound by the action of sodium on mono-

* Wien. Acad. Ber., lxii [2], 605; Zeitschr. f. Chem. [2], vii, 284.

bromophenetol and ethylic bromide, as it forms an explosive blue sodium-compound; the reaction appears to succeed better with magnesium.

A. P.

Action of Zinc on Benzil Tetrachloride and other Chlorine and Bromine Products. By N. ZININ.*

THE chlorides formed by the replacement of hydrogen by chlorine in hydrocarbons are not acted on by zinc; the *additive products* formed from non-saturated hydrocarbons are easily attacked by zinc when dissolved in alcohol or ether, and the compounds from which they are derived are again formed. Thus, naphthalene tetrabromide when acted on by zinc, gives naphthalene; stilbene dibromide yields stilbene; tolene dibromide and dichloride yield tolene; and from the corresponding benzene compounds benzene is formed.

Benzil tetrachloride treated with zinc in hot alcoholic solution, yields two isomeric compounds, $C_{14}H_{10}Cl_2$; the first forms white rhombic plates which melt at 153°, and are soluble in 10 parts of boiling alcohol. The second crystallises in long needles, or six-sided prisms, which melt at 63°, and dissolve in any quantity of boiling alcohol. 10 parts of the tetrachloride yield 2·2—2·4 parts of the first, and 6—5·2 parts of the second compound. They distil undecomposed, are not attacked by zinc, and only slightly by alcoholic potash at 150°; sodium amalgam changes them into tolene.

A. P.

On Benzoyl dioxide and its Reaction with Amylene. By A SPERLICH and E. LIPPMANN.†

THE authors prepare benzoyl dioxide by treating commercial barium peroxide with an equivalent quantity of pure benzoyl chloride. It is then treated with water, and yields benzoyl dioxide having the same properties and crystalline form as described by Brodie.‡

Benzoyl dioxide, heated with amylene and ether up to 100°, yields, besides benzoic acid, an oil which is decomposed by distillation *in vacuo*.

A. P.

On Naphthol Compounds. By JULIAN GRABOWSKI.§

A FURTHER study of the bodies formed by heating polybasic acids with α-naphthol has confirmed the previous supposition that two series of

* Bull. Acad. St. Petersb., xvi, 173; Zeitschr. f. Chem. [2], vii, 284.
† Wien. Acad. Ber., lxii [2], 613; Zeitschr. f. Chem. [2], vii, 285.
‡ Pogg. Ann., 1864, 372. § Deut. Chem. Ges. Ber., iv, 725.

substances are formed by this reaction: the one insoluble in potash, the other soluble, and of corresponding composition to the *phthalein* from phenol.

Oxalic Acid and Naphthol.—On heating a mixture of oxalic acid, naphthol and sulphuric acid for two hours at 110°—115°, a dark mass is obtained only partially soluble in alkali; the portion insoluble is dissolved by hot benzene, and crystallises on cooling in colourless, warty groups. These are a mixture of various substances, but after oft-repeated recrystallisation they are converted into beautiful, colourless, glistening crystals having the composition $C_{21}H_{12}O_2$. This body bears exactly the same relation to carbonic anhydride as the previously described phthalic compound does to phthalic anhydride:

$$C_8H_4O_3 + 2C_{10}H_8O = C_{28}H_{16}O_3 + 2H_2O.$$
$$CO_2 + 2C_{10}H_8O = C_{21}H_{12}O_2 + 2H_2O.$$

The behaviour of the two substances is also identical.

Phthalic Chloride and Naphthol.—On heating a mixture of these two bodies on the water-bath, abundance of hydrogen chloride is evolved, and a green mass remains, partially soluble in cold dilute potash. The dissolved substance is purified by repeated fractional precipitation with hydrochloric acid and recrystallisation from benzene. The small brown crystals so obtained dissolve in potash, with production of a fine blue colour; their composition, when dried at 100°—110°, is $C_{28}H_{18}O_4 + \frac{1}{2}Aq$. Leaving the half molecule of water out of consideration, their formation is analogous to that of the phthalein of phenol:—

$$C_8H_4O_3 + 2C_6H_6O = C_{20}H_{14}O_4 + H_2O.$$
$$C_8H_4O_2Cl_2 + 2C_{10}H_8O = C_{28}H_{18}O_4 + 2HCl.$$

Pyromellitic Acid and Naphthol. — Pyromellitic anhydride and naphthol give when fused together, a black resinous mass, readily soluble in alcohol. The product is purified by solution in potash, in which it dissolves readily with green colour, and fractional precipitation by acid; it is a brown powder of the composition $C_{30}H_{18}O_8$. Here also one molecule of water is separated, but it is again fixed by the second anhydride-group present, converting it into two carboxyls. In proof of this, on heating the new body with resorcin and sulphuric acid, a new compound is obtained containing the elements of resorcin in addition to those of naphthol and pyromellitic anhydride.

H. E. A.

On Sorbite. By Prof. DELFFS.*

AFTER many failures, the author has succeeded in preparing the *sorbite* or *sorbin* of Pelouze. He states that the reason why so many chemists have been unsuccessful in preparing it, is because they have always attempted a previous separation of the malic acid, and have not strictly followed the directions of Pelouze.

He considers that sorbite is not contained ready-formed in the fruits of *Sorbus Aucuparia*, but that it is produced in the expressed juice by a species of fermentation; the malic acid disappearing, while a corresponding proportion of sorbite is produced. Certain it is, that after the sorbite has been crystallised out, no malic acid is to be found in the residue.

A very small quantity of alcohol appears to be produced during the fermentation of the juice, and it seems probable that there is a connection between the disappearance of the malic acid, and the small produce of alcohol on the one side, and the generation of sorbite on the other. Thus, supposing monethylic malate to be produced, the assimilation of one molecule of water, by one molecule of the ether, will yield a formula which exactly represents the composition of sorbite—

$$C_2H_6O + C_4H_4O_4 + H_2O = C_6H_{12}O_6.$$

Further experiments are required to show whether this genesis of sorbite is correct or not.

J. W.

On some Metallic Trichloracetates. By A. CLERMONT.†

THE trichloracetates of barium, strontium, calcium, and sodium were prepared and analysed; they were prepared by adding an excess of trichloracetic acid to the pure carbonates of the metals, and as the solutions must not be heated, they were allowed to evaporate slowly over caustic lime. These salts dried at the ordinary temperature, answered in composition to the general formula $M''(C_2Cl_3O_2)_2 + 6H_2O$ for the salts of the bivalent metals. The composition of the sodium salt was found to be $C_2Cl_3NaO_2 + 3H_2O$.

W. H. D.

On Normal Valeric Acid. By A. LIEBEN and A. ROSSI.‡

THIS acid is produced by distilling normal butyl cyanide (p. 522) with alcoholic potash in a retort with reversed condenser, as long as ammonia continues to escape. On distilling off the alcohol (which contains

* Chem. News, xxiv, 75. † Comptes rendus, lxxiii, 501.
‡ Gazzetta chimica Italiana, i, 239—248.

ammonia and a mixture of mono-, di-, and tri-butylamine, formed as secondary products), dissolving the residual saline mass in water, saturating approximately with sulphuric acid, filtering to separate potassium sulphate, evaporating the filtrate to dryness, and treating the residue with dilute sulphuric acid, the valeric acid is separated and rises as an oil to the surface. This oily liquid washed with a little water and distilled, rejecting the first few drops which are slightly humid, yields pure valeric acid boiling within an interval of 1·5°, and yielding by analysis 58·63 p. c. C., and 9·62 H., the formula $C_5H_{10}O_2$ requiring 58·82 C., and 9·80 H.

Normal valeric acid has an odour more like that of pure butyric acid than that of ordinary valeric acid. When cooled to —16°, it becomes slightly viscous, but does not solidify. A cubic centimetre of this acid dissolves at 16° about 1 c.c. of water; on adding more water, a lower aqueous layer is formed, on which the valeric acid floats, but after the addition of 27 c.c. water to 1 c.c. acid, complete solution takes place. The specific gravity of normal valeric acid referred to water at the same temperature is as follows:—

Temperature	0°	20°	40°	99·3°
Specific gravity ..	0·9577	0·9415	0·9284	0·9034

It boils at 184°—185° (corr.) under a pressure 0·736 met. Ordinary valeric acid prepared by oxidation of optically active amylic alcohol, boils at 175°, and according to the observations of the authors, is identical with the acid of valerian-root.

The difference of constitution of normal and ordinary valeric acid is represented by the formula—

CH_3	H_3C CH_3
CH_2	⟍ ⟋
CH_2	CH
CH_2	CH_2
COOH.	COOH.
Normal.	Ordinary.

That of the latter is established by its synthesis from the butyl cyanide of fermentation (Erlenmeyer),* and by that of isopropylacetic acid (Frankland and Duppa),† the properties of which are exactly similar to those of the valeric acid obtained from optically inactive amyl-alcohol. The constitution of the acid obtained from active amyl alcohol is not yet established.‡

According to Schneider, normal valeric acid is obtained by heating a mixture of ethyl iodide and β-iodopropionic acid with finely divided

* See p. 127 of this volume.

† Ann. Ch. Pharm. Suppl., v, 339.

‡ Ibid., cxlv, 78.

metallic silver; but he does not describe its properties, merely stating generally that it resembles ordinary valeric acid; hence it would appear to be different from that just described.

Normal Valerates.—All the following salts were prepared by saturation, excepting the copper salt, which being but sparingly soluble, was obtained by precipitation. The sodium salt is very soluble in water, and the hot solution gelatinizes on cooling. The *barium-salt*, $Ba(C_5H_4O_2)_2$, is more soluble in hot than in cold water, and its hot saturated solution solidifies on cooling to a mass of unctuous laminar crystals. The dry salt obtained by evaporating the solution at ordinary temperatures and exposing the crystals to the air, is neutral and anhydrous. 100 pts. of a solution saturated at 10° contain 16·906 pts. of the anhydrous salt. The *calcium salt* is obtained by evaporation at ordinary temperatures in small, shining, unctuous laminæ, resembling those of the barium salt; they contain $Ca(C_5H_9O_2)_2 + H_2O$, and give off their water of crystallisation at 100°. This exhibits a maximum of solubility at about 70°, so that it separates from a hot-saturated solution on cooling, and from a cold saturated solution on heating. A solution saturated at about 20° contains 8·0809 per cent. of the anhydrous salt. The *manganous salt*, $Mn(C_5H_9O_2)_2 + H_2O$, forms small faintly rose-coloured crystals, which give off their water at 100°. It is much more soluble in cold than in hot water, and a solution saturated in the cold, deposits when heated, a precipitate (probably of basic salt) which does not redissolve completely on cooling; this decomposition by heat takes place with especial facility in dilute solutions, so that such solutions cannot be concentrated by heat.

The *cupric salt*, $Cu(C_5H_9O_2)_2$, is obtained, by precipitating the sodium salt with cupric sulphate, as an azure-green substance, which partly dissolves when washed and digested with water at ordinary temperatures. The resulting sky-blue solution, when evaporated in a vacuum over sulphuric acid, yields the neutral salt in groups of green microscopic needles; its powder has a lighter colour inclining to sky-blue. This salt is likewise more soluble in cold than in hot water, its solution becoming turbid when heated, and always depositing a small quantity of basic salt, which does not redissolve on cooling, and on evaporating the solution by heat, a residue is obtained consisting chiefly of a sky-blue basic salt. On boiling a dilute solution of the neutral salt, or heating a solution of the basic salt, cupric oxide is precipitated, and valeric acid volatilises with the aqueous vapour. The same decomposition appears also to take place partially at ordinary temperatures. The zinc-salt, $Zn(C_5H_9O_2)_2$, forms thin, shining, transparent laminæ, unctuous to the touch, 100 parts of a solution saturated at 24°—25°, contain 2·54 pts. of the salt; the solution becomes turbid when heated but the precipitate redissolves on cooling.

The chief differences observed between the normal valerates and the salts of ordinary valeric acid are as follows: Ordinary barium valerate is said by some authorities to be uncrystallisable, by others to crystallise with 2 mol. water, whereas normal barium valerate yields anhydrous crystals. Ordinary cupric valerate is described by Trommsdorff as easily soluble, whereas the normal valerate is but slightly soluble. The ordinary zinc-salt decomposes, according to Stolman, at 90°, which is not the case with the normal valerate. We cannot, however, at present attach very great importance to these differences, inasmuch as the salts of ordinary valeric acid have never been very exactly studied. The presence of small quantities of the salts of the optically active valeric acid appears in some instances to prevent the crystallisation of the salts of the inactive acid, and to give them a syrupy character. The authors have not further pursued the examination of the ordinary valerates, since Erlenmeyer is at present engaged in researches of the same nature.

H. W.

On Monochlorocrotonic Acid. By C. SARNOW.*

FUSED trichlorocrotonic acid does not immediately solidify; by dropping the liquid slowly into water and zinc-dust the mixture becomes warm, and the zinc salt of *monochlorocrotonic acid* is produced without any evolution of gas; if, however, too much trichlorocrotonic acid is employed at once, a gas burning with a green flame is evolved, probably containing carbon and chlorine. From the zinc salt thus produced the acid is obtainable by adding hydrochloric or sulphuric acid to its solution; the crude acid thus precipitated is purified by recrystallisation from hot water, in which it easily dissolves; in alcohol and ether it is readily soluble. The acid melts at 94°, and boils at 206°; even in the water-bath it partially sublimes, forming pearly scales and needles; it appears to be identical in every respect with the *monochloro-tetracrylic acid*, obtained by Geuther† by the action of phosphoric chloride on ethyl diacetic acid; its sodium salt treated with water and sodium-amalgam yields an acid free from chlorine, and melting at 72°; this the author has not analysed, but he believes it to be Geuther's *tetracrylic acid.*

From the difficulty with which the chlorine atom in monochlorocrotonic acid is replaced, it is probably in connection with a carbon

* Deut. Chem. Ges. Ber., iv, 731. The author's experiments were commenced before the publication of Krämer's paper (ibid., iii, 703), but have been interrupted in consequence of the war.

† Jenaische Zeitschrift, vi, part 4; and p. 813 of this volume.

atom with which no hydrogen is combined, so that the structure of the acid is—

$$CH_3—CCl=CH—CO.OH,$$
$$\text{or,}\quad CH_3—CH=CCl—CO.OH;$$

thus all attempts to obtain amido- or oxy-crotonic acid from it have hitherto proved fruitless.

Monochlorocrotonic chloride, $C_4H_4ClO.Cl$, is obtained by the action of phosphoric chloride on monochloro-crotonic acid, and is freed from phosphorus oxychloride by redistillation over the dry potassium salt of this acid. It is a clear liquid boiling at 142°, and giving off hydric chloride in the air; its vapours strongly provoke to tears. By the action of the chloride on the potassium salt, the anhydride is apparently formed, but by distillation monochlorocrotonic acid only is obtained, hydric chloride being formed, and a carbonaceous residue being left in the retort.

Monochlorocrotonamide, $C_4H_4ClO.NH_2$, is obtained by the action of aqueous ammonia on the above chloride; it is not very soluble in cold water, but more soluble in hot water, alcohol, or alcohol mixed with ether; pure ether however dissolves it but slightly; it forms pearly plates and crystalline masses, melts at 107°, and boils at 230° to 240°; even at 100° it is volatile to a great extent, and is not perfectly fixed *in vacuo*.

C. R. A. W.

On the Action of Hydrobromic Acid upon Citric Acid. By MARIANO MERCADANTE.*

PULVERISED citric acid dried at 100° was dissolved in three times its weight of hydrobromic acid boiling at 126°, and heated for 12 hours in a flask with reversed condenser. In this manner a crystalline product was obtained, free from bromine, and yielding, when dissolved in alcohol, and treated with gaseous hydrochloric acid, a product which, when treated with water, was resolved into a heavy oil and an aqueous solution of citric acid. No brominated acid was obtained by this reaction.

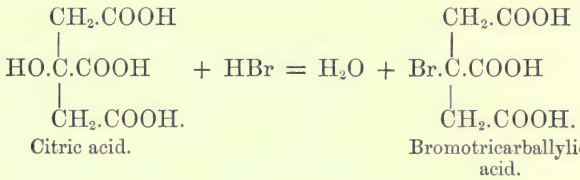
The oil dried with calcium chloride and distilled, boiled almost constantly at 275°; it was slightly yellow, had a characteristic aromatic odour, and yielded by analysis 55·09 p. c. C., and 7·19 H., numbers agreeing nearly with the formula of *aconitic ether*, $C_{12}H_{18}O_6$, which requires 55·81 C., 6·97 H., and 37·22 O. Aconitic ether is said, however, by Crasso† to boil at a much lower temperature, viz., at 236°. The author, therefore, prepared aconitic ether from aconitic acid ob-

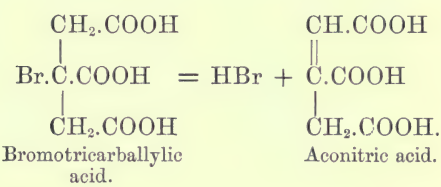
* Gazzetta chimica Italiana, i, 248. † Ann. Chim. Phys. [3], i, 311.

tained by heating citric acid, and thereby obtained an oily liquid which began to boil at 255°, but passed over for the most part between 270° and 275°. This latter portion exhibited all the characters of the product obtained as above by the action of hydrobromic acid on citric acid. It is probable that the aconitic ether examined by Crasso was mixed with itaconic ether, inasmuch as, in preparing aconitic acid by the action of heat on citric acid, it is impossible to obtain a product quite free from itaconic acid.

The action of hydriodic acid on citric acid did not yield definite results. Dessaignes has shown that aconitic acid is formed by boiling citric acid for a long time with hydrochloric acid.

The formation of aconitic acid by the action of hydracids on citric acid consists in the elimination of a molecule of water, and may be represented by the following equations:—





H. W.

Researches on Compounds belonging to the Camphor Group. By J. Kachler.*

A portion of the results obtained by the action of nitric acid on camphor have been already published in this Journal ([2] ix, 560).

The syrupy concentrated mother-liquors of camphoric acid obtained by this means deposit crystals on standing for some months, the mass becoming finally semi-solid; by powerful pressure and recrystallisation from water of the solid portion, pearly minute crystals are obtained (after decolorisation with charcoal), which are very soluble in water, alcohol, and ether, but almost insoluble in benzene and carbon disulphide; the aqueous solution has a sour taste and acid reaction, and decomposes metallic carbonates, forming two classes of salts, in which

* Ann. Chem. Pharm. clix, 281.

H_2 and H_3 are replaced by metals. The acid itself, when air-dry, loses no water at 100°, and has then the composition $C_9H_{14}O_6$; heated to 110° it begins to fuse and loses water, giving an anhydrous compound which melts at 115°, and distils unaltered at a slightly higher temperature; both the distilled product and the substance melting at 115° give numbers agreeing with the formula $C_9H_{12}O_5$; the author proposes to call it *camphoronic acid.*

The bibasic ammonium salt loses both water and ammonia at 100°; dried *in vacuo* it contains $C_9H_{10}(NH_4)_2O_5 + H_2O$. The bibasic barium and zinc salts are obtained by treating the acid with the carbonates of these metals; dried at 170° their compositions are $C_9H_{10}Ba''O_5$ and $C_9H_{10}Zn''O_5 + H_2O$, the latter not losing its water even at 200°.

By boiling a solution of the acid saturated with ammonia with barium chloride, an insoluble sandy crystalline powder is precipitated, which will bear washing with water; this is a tribasic salt, and has the composition $(C_9H_9O_5)_2Ba''_3 + 2H_2O$, the water of crystallisation being lost at 185°; the formation of this sandy precipitate on boiling serves as a qualitative test for the acid, and also as a means of preparing the pure acid from the syrupy mother-liquors in the first instance, by decomposition of the salt with dilute sulphuric acid and exhaustion with ether.

A tribasic calcium salt $(C_9H_9O_5)_2Ca''_3 + 4H_2O$, and two copper salts, $(C_9H_9O_5)_2Cu_3 + 4H_2O$, and $(C_9H_9O_5)_2Cu_3 + 2H_2O$, have also been analysed; the silver and lead salts are decomposed on washing, and the potassium and sodium salts are so soluble as not to be capable of being brought into a condition fit for analysis.

An alcoholic solution of the acid saturated with gaseous hydrogen chloride, deposits an oil from which, by distillation, a mono-ethyl ether can be isolated; it boils at 302°, and has the composition $C_9H_{11}(C_2H_5)O_5$.

The calcium salt, mixed with quicklime and distilled, gives a thick product, from which by rectification a clear and perfectly volatile substance of composition, $C_7H_{12}O$, is isolable, formed by the reaction—

$$C_9H_{12}O_5 = 2CO_2 + C_7H_{12}O.$$

This formula requires a vapour-density = 3·86; the numbers found in two determinations were 3·69 and 3·74.

Heated with three times its weight of caustic potash, camphoronic acid is completely decomposed; on distillation of the product with dilute sulphuric acid, a distillate containing *butyric acid* is obtained, the reactions being $C_9H_{12}O_5 + H_2 + H_2O = 2C_4H_8O_2 + CO_2$ (?). The silver salt was analysed, and the boiling point of the acid (extracted by ether) found to be between 155° and 160°.

By heating to 130° for two hours a mixture of one molecule of air-

dried camphoronic acid ($C_9H_{12}O_5 + H_2O$) and two molecules of bromine, a large quantity of hydrogen bromide is formed, and an acid which crystallises in fine large crystals, free from bromine, and containing $C_9H_{12}O_6 + H_2O$, the water of crystallisation being lost at 100°. These crystals belong to the monoclinic system, and give the following crystallographic numbers:—

$$a : b : c = 1{\cdot}49418 : 1 : 0{\cdot}98075.$$
$$ac = 86^{\circ}{\cdot}50'.$$

Observed faces.. 100 . 001 . 101 . 110 . 010 . $\bar{2}05$.

The author calls this new acid *oxycamphoronic acid*, as it is formed by the reaction $C_9H_{12}O_5 + H_2O + 2Br = 2HBr + C_9H_{12}O_6$; when anhydrous it begins to melt at 210°, and is volatile without decomposition; it is readily soluble in water, alcohol, and ether, and decomposes carbonates; salts in which H_1, H_2, H_3, are replaced have been obtained, the majority belonging to the second class; indeed, the acid potassium salt, and the tribasic lead-salt, are the only representatives of the other two classes.

Oxycamphoronic acid is not formed from anhydrous camphoronic acid by the action of bromine, nor is any bromine-substitution compound obtainable from either acid. Fused caustic potash acts on both acids alike; both are but little attacked by nitric acid, and are unaltered by treatment with sodium amalgam.

The author doubts the existence of Schwanert's camphresinic acid, $C_{10}H_{14}O_7$; by the oxidation of camphoric acid with nitric acid camphoronic acid is produced, an amorphous sour syrup being obtained, which presents all the characters of Schwanert's acid, but which is principally camphoronic acid, this acid being obtainable from it by the formation of the tribasic barium salt, &c.

C. R. A. W.

On the Synthesis of Piperonylic Acid, and a New Mode of Preparing Protocatechuic Aldehyde. By RUDOLPH FITTIG and IRA REMSEN.*

THE previous researches on piperonylic acid and its aldehyde have rendered it probable that the structural formulæ of these two substances are—

the two bodies being respectively methylene-protocatechuic acid and aldehyde. In order to prove this by synthesis, 1 molecule of pure

* Zeitschr. f. Chem. [2], vii, 289.

protocatechuic acid, 3 of caustic potash, and $1\frac{1}{2}$ molecule of methylene iodide were sealed up together and heated for several hours, at first in the water-bath, and finally to 140° in an air-bath; the nearly black contents of the tube were treated with alcohol; and the extract thus obtained was heated with potassium hydrate for some time to decompose any methylene-ether of methylene-protocatechuic acid; finally hydrochloric acid was added, and the filtrate from the brown amorphous precipitate produced was evaporated. Crystals were thus obtained, which, after recrystallisation, treatment with animal charcoal, and sublimation, possessed all the characters of piperonylic acid, melted at the same temperature, 227°, and were in every respect indistinguishable from that acid.

Just as piperonylic acid, when heated with dilute hydrochloric acid, splits up into carbon and protocatechuic acid, so piperonal when heated to 200° with very dilute acid (10 or 12 volumes water to 1 of concentrated acid), splits up, forming protocatechuic aldehyde and carbon, thus:—

$$C_6H_3\begin{cases}\diagup O \diagdown \\ \text{—} O \diagup \end{cases}CH_2 \;\; \diagdown CHO \;=\; C_6H_3\begin{cases}\diagup OH \\ \text{—} OH \\ \diagdown CHO\end{cases} + C.$$

C. R. A. W.

On Ethylene-protocatechuic Acid. By Rud. Fittig and Thomas Macalpine.*

On heating a sealed tube containing a mixture of 3·5 parts protocatechuic acid, 10 of ethylene dibromide, and 4·5 of solid potassium hydrate in a water-bath for several hours, with occasional shaking, a product is obtained which, by exhausting with alcohol, treatment with potassium hydrate and hydrochloric acid in succession, extraction of the acid liquid thus obtained with ether, evaporation, recrystallisation, and sublimation, yields ethylene-protocatechuic acid,

$$C_6H_3\begin{cases}\diagup O \diagdown \\ \text{—} O \diagup \end{cases}C_2H_4 \;\; \diagdown CO.OH.$$

This new acid much resembles piperonylic acid, but is somewhat more soluble in hot water; in alcohol it dissolves almost in all proportions; it melts at 133°, and sublimes in shining prisms at a higher temperature; its calcium and barium salts are crystalline, and, like piperonylic acid, it gives a yellow precipitate with ferric chloride.

C. R. A. W.

* Zeitschr. f. Chem. [2], vii, 291.

On the Action of molten Potassium Hydrate on Sulpho-oxybenzoic Acid. By IRA REMSEN.*

WHEN sulphobenzoic acid is fused with potassium hydrate, it has been shown (p. 369) that *two* acids are produced, *i.e.*, that the so-called oxybenzoic acid is a mixture derived from two isomeric sulphobenzoic acids. On preparing a perfectly pure barium salt of one of these sulphobenzoic acids, converting it into potassium salt, and fusion with potassium hydrate, pure oxybenzoic acid is obtained.

Similarly, when sulpho-oxybenzoic acid is fused with potassium hydrate, *two* acids are produced, viz., protocatechuic, and another one, which melts at 189°, and gives no reaction with ferric chloride. Crystallised from water, this acid forms large, compact, apparently quadratic tables, which contain water of crystallisation lost at 140°; it is less soluble in water than protocatechuic acid.

Hence no conclusions as to the relation in structure between protocatechuic and oxybenzoic acids can be drawn from the production of the former acid from the sulpho-acid of the latter.

C. R. A. W.

On Isomeric Sulphosalicylic Acids. By IRA REMSEN.†

WHEN pure salicylic acid is dissolved in ordinary sulphuric acid by the aid of very little heat, and the product is neutralised with calcium carbonate, filtered from gypsum, precipitated by potassium carbonate, decolorised by animal charcoal, and allowed to crystallise, there are obtained prismatic crystals which have the composition $C_7H_4O_6SK_2 + 2H_2O$; the water of crystallisation is not lost below 190°, the substance beginning to decompose at 200°; from the mother-liquors of this salt, however, there is obtainable another salt which crystallises in quadratic tables very different from the prisms of the former salt; it is much more soluble, and contains $C_7H_4O_6SK_2 + 1\frac{1}{2}H_2O$, the water of crystallisation being first lost at 180°, and decomposition commencing at 190°. Neither salt is altered in characters by further recrystallisation; fused potassium hydrate does not act on these compounds so readily as on compounds which contain fewer substituted groups; one will doubtless yield the known oxysalicylic acid.

C. R. A. W.

On the Oxidation of Toluene-sulphuric Acids. By IRA REMSEN.‡

CRUDE toluene-sulphuric acid (mixture of ortho- and para-acids) was treated with potassium dichromate and sulphuric acid and gently heated

* Zeitschr. f. Chem. [2], vii, 294. † Zeitschr. f. Chem. [2], vii, 296.
‡ Zeitschr. f. Chem. [2], vii, 297.

to start the action; much heat was evolved, and gas was liberated continuously for about an hour, when the oxidation was completed; the product was then precipitated by chalk, and the filtrate treated with baryta-water to precipitate chromic acid, and evaporated to dryness. The residue gave, with sulphuric acid and alcohol, a mixture of acids, one of which yielded a barium salt much more soluble than that from the other; the latter was found to be pure para-sulphobenzoic acid; the former was not analysed, but was believed to be ortho-sulphobenzoic acid, inasmuch as the mixture of the two acids converted into potassium salts and fused with potassium hydrate, yielded para-oxybenzoic acid, and also salicylic acid. Hence it appears that the methyl group in each of the two toluene-sulphuric acids was oxidised, and that (contrary to expectation) the ortho-acid was not completely oxidised and destroyed.

The acid sodium-salt, and the neutral barium and calcium salts of para-sulphobenzoic acid have been prepared; the acid itself is not volatile, melts at about 200°, and is but little soluble in water.

It is proposed to treat xylene-sulphuric and mesitylene-sulphuric acids in the same way, so as to obtain an oxydibasic and an oxytribasic acid.

C. R. A. W.

Miscellaneous Observations. By A. Engelhardt and P. Latschinow.*

Derivatives of Diphenyl.—This hydrocarbon may be prepared by mixing 780 grams of benzene, 25 grams of iodine, and 1,256 grams of bromine. The reaction goes on quietly, but towards the end the heat of the water-bath has to be applied. On distillation the portion boiling below 159° is collected separately, and, after drying and removing all traces of hydrobromic acid, 150 grams of sodium are added. If the reaction does not begin by itself, it is started by gently heating, but as soon as it begins, the mixture has to be well cooled. The products of the reaction consist of excess of benzene, of diphenyl (of which 120 grams were obtained), and of a liquid having a very high boiling point. In the retort there remains, besides sodium iodide, a black solid which can be volatilised by very strong heat.

Monosulpho-diphenylic acid, $C_{12}H_9SO_3H$, is formed by heating 50 grams of the hydrocarbon with 70 grams of sulphuric acid until water and diphenyl escape.

The liquid is now diluted with water and incompletely neutralised with potassium carbonate. On cooling, the potassium salt crystallises out, whilst the more soluble salt of the disulpho-acid remains in the mother-liquor.

* Zeitschr. f. Chem., xiv, 259—263.

$C_{12}H_9SO_3K + H_2O$ is readily soluble in boiling water; on cooling, the solution solidifies to a magma of very fine hair-shaped crystals, which after some time change into a heavy powder. $(C_{12}H_9SO_3)_2Ba$ is obtained by adding barium chloride to a solution of the potassium salt, as a precipitate which crystallises from boiling water in small scales. $(C_{12}H_9SO_3)_2Ca$ is also prepared by precipitation, and crystallises from a hot solution in long, thin, shining leaves. On heating the potassium salt until it acquired a brown colour, water and diphenyl were given off, and $C_{12}H_8(SO_3K)_2$ was left behind.

Fittig's disulpho-phenylic acid is formed by using an excess of sulphuric acid. The potassium salt, $C_6H_8(SO_3K_2) + 2\frac{1}{2}H_2O$, crystallises in large laminæ. Its solution is precipitated by barium chloride in the cold, but by calcium chloride only when hot.

By distilling potassium disulphophenylate with potassium cyanide, a colourless solid nitrile was formed, from which, by the action of alcoholic potash, a crystallised salt ($C_{12}H_8(CO_2K)_2$?) was obtained. By fusing the potassium salt of the disulpho-acid with caustic potash and adding hydrochloric acid to the solution of the fused mass, a crystalline precipitate was formed, which appeared to have the composition $C_6H_4(SO_3K).C_6H_4OH$, as on distilling it, the crystalline phenol, $C_{12}H_8(OH)_2$, is formed, probably thus—

$$2C_6H_4(SO_3K)C_6H_4OH = C_{12}H_8(OH)_2 + C_{12}H_8(SO_3K)_2.$$

On Bromo-α-Sulphothymolic Acid.—The brominated acid is formed by adding bromine to a cold solution of the potassium salt of the sulpho-acid. The potassium salt, $C_{10}H_{12}Br(SO_3K)O$, crystallises from hot water in long needles. The anhydrous barium salt is sparingly soluble in cold water, and crystallises from a boiling solution in thin silky needles.

By heating the solution of the potassium salt on the water-bath with a little nitric acid, *dinitrothymol* is formed, the ammonium-salt of which crystallises from hot dilute ammonia in orange-red needles. By adding barium chloride to its concentrated solution, a yellow precipitate is formed, which crystallises from a boiling solution in thin shining-red needles, $C_{10}H_{11}(NO_2)_2BaO + 1\frac{1}{2}H_2O$. When the aqueous solution of barium α-sulphothymolate is heated with nitric acid, dinitrothymol and barium sulphate are formed.

On oxidising the α-sulpho-acid with chromic acid, a quinone (Lallemand's thymoil) and acetone are formed.

On Chrysanisic Acid.—By treating nitranisic acid with a mixture of nitric and sulphuric acids, chrysanic acid, dinitrophthalic acid, picric acid and a new acid are formed. The dinitrophthalic acid is as sparingly soluble in water as chrysanisic acid. It crystallises from a hot solution in colourless rhombic plates. The ammonium salt forms thin

yellow needles, readily soluble in water. The barium salt is nearly insoluble in boiling water. The fourth acid is much more readily soluble, and forms also yellow salts.

C. S.

Communications from the University Laboratory of Goettingen. By H. HUEBNER.*

1. *On the Derivatives of β-Parabromo-sulphotoluene.*—By F. C. G. MUELLER.—By the action of sodium amalgam on this compound a toluene-sulphonic acid† is formed, which is an ortho-compound, as its amide differs from the known amides of the meta- and the para-acids. It melts at 91°—92°, and crystallises from a hot concentrated aqueous solution at 30° in very large, transparent plates, but from a more dilute solution it separates below 20° in short filaments.

Nitro-β-Parabromotoluene-sulphonic Acid is obtained by adding finely powdered dry barium β-parabromotoluene-sulphonate to warm fuming nitric acid. It is soluble in water, alcohol, and ether, and crystallises in small deliquescent needles, which are grouped in stars. The acid and its salts have an intensely bitter taste. Most of the salts form microscopic but well defined crystals.

The barium salt, $(C_6H_2BrNO_2 . CH_3.SO_3)_2Ba + 2aq$, separates from dilute aqueous solution in warty hard crystals; from a more concentrated in flat needles grouped in stars. The lead salt $(C_6H_2BrNO_2 . CH_3 . SO_3)_2Pb + 2aq$, crystallises from a hot solution in shuttle-shaped needles. The anhydrous potassium salt crystallises like the lead salt. The sodium salt, $C_6H_2BrNO_2.CH_3SO_3Na + aq$, forms long tufted needles. The anhydrous calcium salt is the only one which does not crystallise well.

2. *On the Action of Phosphorus Pentachloride upon Orthobromobenzoic Acid.*—By the same.—The two compounds act easily on each other, *bromobenzoyl chloride*, $C_6H_4Br.COCl$, being formed, a colourless, strongly refracting liquid, boiling at 239°, and smelling like stewed turnips. On heating it with phosphorus pentachloride in sealed tubes it is acted upon only at 200°, the product being a mixture of different substances, and not as might be expected, *bromobenzol-trichloride* $C_6H_4Br . CCl_3$.

3. *On Sulpho- and Sulphonitro-dibromobenzene.*—By R. DOUGLAS WILLIAM. To obtain sulpho-dibromobenzene, dibromobenzene was dissolved in Nordhausen sulphuric acid, the liquid diluted with water, neutralized with lime, the calcium salt decomposed by sulphuric acid, and the sulpho-acid dissolved out with alcohol. A better method, however, is to decompose the lead salt with sulphuretted hydrogen.

* Zeitschr. f. Chem., xiv, 299—305. † Ibid., N.F., vii, 14.

The sulpho-acid crystallises in silky needles, which gradually change into compact plates. It contains 2 mol. of water of crystallisation, and melts at about 117°, becoming brown at the same time. The following salts were analysed:—

$(C_6H_3Br_2SO_3)_2Ca + 4H_2O$, forms long colourless needles, very soluble in water; $C_6H_3Br_2SO_3Ag + 3H_2O$, transparent needles, and very soluble. $(C_6H_3Br_2SO_3)_2Pb + 3H_2O$, crystallises from a saturated solution in fine, long, six-sided prisms, which change after some time into large, compact, rhombic tables. $(C_6H_3Br_2SO_3)_2Ba + 2H_2O$, forms four-sided tables, very soluble; $C_6H_3Br_2SO_3Na + 1\frac{1}{2}H_2O$, long needles, very soluble; $C_6H_3Br_2SO_3K + H_2O$, fine, very soluble needles.

Dibromonitrosulphobenzene, $C_6H_2Br_2NO_2SO_3H$, is obtained as a viscous mass on boiling dibromosulphobenzene with fuming nitric acid. $C_6H_2Br_2NO_2SO_3K + 2\frac{1}{2}H_2O$ forms small needles, soluble in alcohol and water; $(C_6H_2Br_2NO_2SO_3)_2Ba + 2\frac{1}{2}H_2O$, groups of small needles. $(C_6H_2Br_2NO_2SO_3)_2Cu + H_2O$, is very soluble in water, alcohol, and ether; on evaporating the latter solution, it remains as a syrup, in which crystalline nodules gradually appear. $(C_6H_2Br_2NO_2SO_3)_2Pb + 2H_2O$ forms very small, reddish needles, sparingly soluble in water. The strontium salt is very soluble, and crystallises in microscopic needles.

4. *On Bromo-sulphotoluenes.* By H. Huebner.

C. S.

Action of Chlorine on Aldehyde. By Ad. Wurtz.*

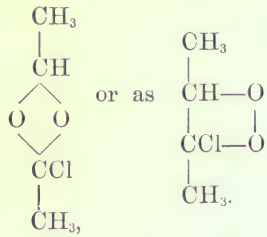
The author's previous statements† that acetyl chloride, and the compound $C_4H_7ClO_2$ (obtainable by direct combination of acetyl chloride and aldehyde), are produced by the action of chlorine on aldehyde, having been disputed by Krämer and Pinner, fresh experiments have been made, the results of which perfectly corroborate those previously obtained.

By passing chlorine through an ice-cold mixture of carbon perchloride and one-tenth of its weight of aldehyde, in sunshine, till the liquid becomes strongly yellow, a product is obtained, which on agitation with mercury and distillation, gives off hydrogen chloride, and yields, after fractionating several times, a liquid boiling below 70°, and another boiling at about 120°. The first is a mixture of acetyl chloride and carbon perchloride, difficult to separate completely by distillation alone; water produces acetic and hydrochloric acids, with evolution of heat, whilst aniline gives acetanilide, melting at 113°, and giving correct numbers on analysis.

The liquid boiling near 120° has the formula $C_4H_7ClO_2$; on treating

* Comptes rendus, lxxiii, 528. † Ann. Chim. Phys. [3], xlix, 58.

it with water, hydrochloric and acetic acids, are produced, and apparently aldehyde, from which the author concludes that this substance has not the composition $CH_2Cl-CHO + CH_3-CHO$, as Krämer and Pinner contend, but that it contains the elements of acetyl chloride and aldehyde coalesced, either as—



C. R. A. W.

On the Aldehyde of the Naphthalene Group. By J. BATTERSHALL.*

AN intimate mixture of calcium formate and naphthoate was distilled at a very high temperature; the distillate contained much naphthalene and also naphthoïc aldehyde, which was obtained in a pure state by shaking with sodic bisulphite and washing the resulting crystalline compound with ether till it became colourless, and finally by decomposition of the white crystals with soda ley and distillation; the aldehyde, $C_{11}H_8O$, passes over in colourless oily drops along with water. In the pure state it is a somewhat thick liquid of peculiar faint smell, and becomes coloured on exposure to air; it is heavier than water, boils at about 280°, but cannot be distilled without forming a small quantity of condensation products of higher boiling point; with steam, however, it can be volatilized readily, and without undergoing any change.

Iso-naphthoic acid (from potassium β-napthyl-sulphate) furnishes by similar treatment an aldehyde of very similar physical characters.

C. R. A. W.

On the Oxidation of the Ketones. By A. POPOFF.†

Methylphenyl ketone, $CH_3-CO-C_6H_5$, boiling point 199°—200°, prepared by the action of zinc-methyl on benzoyl chloride, was oxidized (2 parts) with a mixture of 4 parts potassium bichromate, $5\frac{1}{2}$ parts sulphuric acid, and 20 parts water. Energetic reaction and immediate evolution of carbonic anhydride took place. On subsequently distilling, crystals were deposited in the condenser, which were recognized as benzoic acid, and a further quantity of the same was isolated in the form of calcium salt from the acid distillate. No other acid could be detected either in the residue or in the distillate.

* Zeitschr. f. Chem. [2], vii, 292. † Deut. Chem. Ges. Ber., iv, 720.

Ethylphenyl ketone, boiling point 208°—212°, from zinc ethyl and benzoyl chloride, was similarly oxidized. Carbonic anhydride was evolved, but in small quantity only. The silver salts obtained by fractionally saturating the acid distillate, contained respectively 51·9 and 55·5 per cent. silver; silver benzoate contains 47·1 per cent., and a mixture of equal molecules of silver acetate and benzoate contains 54·5 per cent. silver. The presence of both acids was, moreover, placed beyond all doubt by converting the portion of the distillate first passing over into potassium salt, and heating this with arsenic acid, when the smell of cacodyl was at once apparent. From the latter portion of the distillate, crystalline needles were obtained by extraction with ether, melting at 121·5°, and otherwise possessing all the characteristic properties of benzoic acid.

It appears, then, that methylphenyl ketone is resolved by oxidation into benzoic acid and carbonic anhydride; ethylphenyl ketone into benzoic and acetic acids. In both cases the CO group remains combined with the aromatic residue, the fatty group alone becoming oxidized.

H. E. A.

Researches on the Uric Acid Group. By M. Nencki.*

The object of the author's experiments has been to obtain sulpho-derivatives of uric acid, in the hope that it would then be possible, by the subsequent removal of the sulphur, to synthesize uric acid.

A mixture of 2—3 grms. sulpho-urea and the equivalent quantity of alloxan, was heated with concentrated alcoholic solution of sulphurous anhydride in sealed tubes to 100° for about five hours. The product was purified by repeated treatment with concentrated ammonia to remove uranil; dissolution in caustic soda, rise of temperature being carefully avoided; filtration; precipitation with solution of ammonium chloride, to remove sulphur; and recrystallisation from very concentrated hydrochloric, or better hydrobromic acid, from which it separates on cooling in slender needles, concentrically grouped, of the composition $N_4C_5O_3SH_6$. This new body, which the author names *sulpho-pseudouric* acid, is probably formed according to the equation:—

$$N_2C_4O_4H_2 + N_2CSH_4 = N_4C_5O_3SH_6 + O.$$

It is insoluble in water and ammonia, difficultly soluble in hydrochloric, but more readily in hydrobromic and sulphuric acids, being reprecipitated on the addition of water. All attempts to remove the sulphur from it have been unsuccessful. It is readily soluble in the fixed alkalies, even in the cold; on warming, the solution becomes yellow, and then contains the alkaline salt of a new body, precipitable

* Deut. Chem. Ges. Ber., iv, 722.

from the very dilute solution by hydrochloric acid in the form of silky, glistening, microscopic plates, which on analysis gave numbers agreeing both with the formula of hydrated sulphoalloxantin, $C_8N_4S_2O_7H_8 + 2aq$, and of sulphodialuric acid, $C_4N_2SO_3H_4 + 1\frac{3}{4}aq$. The instability of this substance renders a determination of the water of crystallisation difficult.

On heating sulphopseudouric acid with twice its weight of concentrated sulphuric acid to 150°, evolution of sulphurous anhydride takes place; the temperature was gradually raised to 200°, and the heating continued until the evolution of gas ceased. The purified product gives numbers agreeing with the formula $N_4C_5SO_2H_6$, and bears a great resemblance to xanthine in all its reactions; it is, therefore, highly probable that it is the corresponding sulpho-compound.

H. E. A.

Formation of Secondary Monamines by the action of Bases of the formula $C_nH_{2n-7}.H_2N$.—*On Naphthylamine Hydrochloride.* By CH. GIRARD and G. VOGT.*

WHEN aniline and naphthylamine hydrochloride are heated to 280° in sealed vessels for about thirty-six hours, the following reaction ensues:—

$$\left.\begin{matrix}C_{10}H_7\\H\\H\end{matrix}\right\}N.HCl + \left.\begin{matrix}C_6H_5\\H\\H\end{matrix}\right\}N = \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N.HCl + \left.\begin{matrix}C_{10}H_7\\C_6H_5\\H\end{matrix}\right\}N.$$

From the products of the reaction, *naphthyl-phenylamine* is isolated by treatment with water, which leaves the base as an oily liquid which soon solidifies; by washing, pressure between bibulous paper, and crystallisation from alcohol, it is obtained in small crystals fusible at 60°, and soluble in alcohol, benzene, and ether, its solutions exhibiting dichroism; it distils unchanged at about 315° at 528 mm. pressure.

Its hydrochloride is obtained in small crystals by passing hydrochloric acid gas into a solution of the base in benzene; by ebullition of the benzene liquid it is mostly decomposed; alcohol also partly decomposes it, whilst water resolves it wholly into hydrogen chloride and the free base.

Cresyl-naphthylamine $\left.\begin{matrix}C_{10}H_7\\C_7H_7\\H\end{matrix}\right\}N$, is similarly obtained by the action of toluidine on naphthylamine hydrochloride at 280° for 36 hours; it melts at 79° and distils at 290° at 528 mm. pressure; its hydrochloride is obtainable by the same means as those used for phenyl-naphthylamine, and is also decomposed by water.

* Comptes rendus, lxxiii, 627.

Methyl-diphenylamine is similarly obtained by the action of methyl aniline on aniline hydrochloride at 280° for 36 hours; at ordinary temperatures it is liquid; it distils at 270° at 528 mm. pressure: heated with carbon sesquichloride it yields a magnificent blue-violet colouring matter.

C. R. A. W.

Methylisation of the Phenyl-group in Aniline. By A. W. HOFMANN and C. A. MARTIUS.*

WHEN pure aniline boiling at 182°, is converted into hydrochloride, and this salt digested with pure methylic alcohol at a temperature of from 280°—300°, the following reactions take place:—

$$\left.\begin{matrix}C_6H_5\\H_2\end{matrix}\right\}N,HCl + \left.\begin{matrix}CH_3\\H\end{matrix}\right\}O = \left.\begin{matrix}C_6H_5\\CH_3\\H\end{matrix}\right\}N,HCl + H_2O.$$

$$\left.\begin{matrix}C_6H_5\\CH_3\\H\end{matrix}\right\}N,HCl + \left.\begin{matrix}CH_3\\H\end{matrix}\right\}O = \left.\begin{matrix}C_6H_5\\CH_3\\CH_3\end{matrix}\right\}HCl \quad + H_2O.$$

This reaction has been employed for some years in the industrial factories of aniline colours; on repeating this operation on a somewhat large laboratory scale (10 kilogs. aniline salt employed and 6 kilogs. methyl alcohol) there was ultimately obtained, besides a mixture of methyl- and dimethyl-aniline boiling at about 200°, a quantity of a basic oil of higher boiling point. In the anticipation that this oil contained bodies formed by reactions analogous to those by which the methyl-aniline had been produced, but where the hydrogen of the phenyl group had been further replaced, the mixture of hydrochlorides of methyl- and dimethyl-aniline arising from the first operation was again digested with excess of methyl alcohol at 300°; the quantity of high boiling basic oil thus obtained was much increased, and its range of boiling point heightened.

Fractional distillation alone does not separate the several components of this oily mixture of bases. By treatment with methyl iodide, the fractions thus obtained furnished crystallised iodides which gave strongly alkaline hydroxyl-compounds with silver oxide, showing that the bases were tertiary. On crystallising these iodides by solution in alcohol and precipitation with ether, converting the purified iodides into chlorides by treatment with silver chloride, and partial precipitation with platinum chloride, or crystallisation of the platinum salts from boiling water, substances were finally obtained yielding analytical

* Deut. Chem. Ges. Ber., iv, 220.

numbers which proved that the hydrogen of the phenyl group had actually been replaced by reactions similar to the following:—

$$\left.\begin{matrix}C_6H_5\\CH_3\\CH_3\end{matrix}\right\}N,HCl + \left.\begin{matrix}CH_3\\H\end{matrix}\right\}O = H_2O + \left.\begin{matrix}C_6H_4(CH_3)\\CH_3\\CH_3\end{matrix}\right\}N,HCl.$$

$$\left.\begin{matrix}C_6H_4(CH_3)\\CH_3\\CH_3\end{matrix}\right\}N,HCl + \left.\begin{matrix}CH_3\\H\end{matrix}\right\}O = H_2O + \left.\begin{matrix}C_6H_3(CH_3)_2\\CH_2\\CH_3\end{matrix}\right\}N,HCl.$$

and so on; thus the following series of bases has been obtained:—

Dimethyl-aniline	$\left.\begin{matrix}C_6H_5\\(CH_3)_2\end{matrix}\right\}N.$
Dimethyl-toluidine	$\left.\begin{matrix}C_6H_4(CH_3)\\(CH_3)_2\end{matrix}\right\}N.$
Dimethyl-xylidine	$\left.\begin{matrix}C_6H_3(CH_3)_2\\(CH_3)_2\end{matrix}\right\}N.$
Dimethyl-cumidine	$\left.\begin{matrix}C_6H_2(CH_3)_3\\(CH_3)_2\end{matrix}\right\}N.$
Dimethyl-cymidine	$\left.\begin{matrix}C_6H(CH_3)_4\\(CH_3)_2\end{matrix}\right\}N.$

The final body $\left.\begin{matrix}C_6(CH_3)_5\\(CH_3)_2\end{matrix}\right\}N$, has not yet been proved to exist among the products of the action of methylic alcohol on aniline hydrochloride.

Experiments to decide whether the dimethyl-xylidine thus produced is identical with that arising from the methylisation of xylidine; whether the dimethyl-toluidine belongs to the toluidine or paratoluidine series; whether it is possible similarly to ethylize, amylize, &c., the phenyl group, and so on, are promised, and some are already in progress.

In all probability the equations given above only represent the end-reactions taking place; no doubt methyl chloride is formed, and is the true agent which brings about the substitution.

C. R. A. W.

On some Derivatives of Orthotoluidine. By E. Wroblevsky.*

The orthotoluidine employed was prepared from orthonitroparatoluidine; but instead of converting the azo-compound into sulphate, the nitrotoluidine was added in small portions to alcohol saturated with nitrous acid. The reaction proceeds in the cold, and the yield is not smaller than that given by the earlier process. On passing bromine vapour into hydrochloric acid solution of orthotoluidine, the bromine

* Zeitschr. f. Chem. [2], vii, 271–273.

is absorbed at once, and white flakes are deposited. These white flakes consist of *tribromorthotoludine* $C_7H_4BrBr_{m2}NH_{2o}$, difficultly soluble in alcohol, from which it crystallises in beautiful long needles. It melts at 97°, and does not combine with acids. When tribromotoluidine is added to alcohol saturated with nitrous acid, an energetic reaction ensues, in consequence of which tribromotoluene is formed, together with aldehyde and nitrogen. *Tribromotoluene*, $C_7H_5BrBr_{m2}$, crystallises from benzene in long silky needles, which melt at 70° and boil at 290° without decomposition. It yields a crystallisable nitro-compound, $C_7H_4NO_2Br_3$, which melts at 215°.

It is noteworthy that a dibromo-derivative only is obtained from para- and meta-toluidine, while orthotoluidine furnishes a tribromo-derivative. Dibromorthotoluidine, $C_7H_5Br_{m2}.NH_{o2}$, is obtainable by the action of potash on dibromacetoorthotoluidine; it crystallises in silky needles, melts at 92·5°, and does not combine with acids. From this dibromotoluidine a new dibromotoluene was obtained, isomeric with the five dibromotoluenes already known.

In a former communication, the author, by comparing the methods of preparation, elucidated the structure of five isomeric forms of dibromotoluene, which left only one modification with the structure 1 : 3 : 5 to be prepared. His expectation of obtaining this body from dibromorthotoluidine is confirmed by experiment. This dibromotoluene, $C_7H_6Br_{m2}$, is a liquid which does not crystallise at − 20°; its specific gravity at 22° = 1·812; it boils at 246°. By nitration, it yields *nitro-dibromotoluene*, $C_7H_5NO_2Br_{m2}$, a body melting at 79°.

A tabular view of the six dibromotoluenes is given, showing the differences which exist in their melting and boiling points, and specific gravities, or in the melting points of their nitro- and amido-derivatives.

The author considers that further experiments are necessary before accepting Victor Meyer's views respecting the salicylic and ortho-benzoic acid series, viz., that salicylic acid belongs to the ortho-series (1 : 2), and oxybenzoic acid to the meta-series (1 : 3).

W. H. D.

On Monacetorosaniline. By C. Becherhinn.*

This substance is obtained by the action of acetamide on rosaniline hydrochloride, with simultaneous formation of ammonia: $C_{20}H_{19}N_3 + C_2H_3O.NH_2 = C_{20}H_{18}(C_2H_3O)N_3 + NH_3$. 200 grams of fuchsine are heated with 40 grams of acetamide up to 180°−185° until no more ammonia is evolved; the undecomposed fuchsine is removed with water, and the product is dissolved in alcohol, and precipitated with

* Wien. Acad. Ber. [2], lxii, 412; Zeitschr. f. Chem. [2], vii, 285.

hydrochloric acid. The monacetorosaniline hydrochloride is purified by washing and repeated precipitation.

Monacetorosaniline is a chocolate-brown powder, soluble in alcohol, with a red colour, insoluble in water, ether, and alkalies, and having the composition $C_{20}H_{16}(C_2H_6O)HCl$. From its alcoholic solution it is obtained by evaporation, with a dark bronze metallic lustre, which appears dark blue by transmitted light. Its solutions are precipitated by carbonic anhydride and by alkalies, whilst hydrochloric acid in excess colours it dark green. It does not fix well on fibres. The free base, $C_{20}H_{18}(C_2H_3O)N_3$, is obtained by caustic alkalies as a red-brown powder, which by oxidation in the air changes to a red-violet; it is easily soluble in alcohol, chloroform, and carbon disulphide, with a red-brown colour, but is insoluble in ether, water, and in alkalies. From its alcoholic solution it is obtained by evaporation as a red-brown vitreous mass. When heated to 130° with alcoholic potash, it yields rosaniline and acetic acid. With sodium-amalgam, it gives a yellow reduction-product, the hydrochloride of which is soluble in alcohol with a blue colour, and is precipitated with ether.

A. P.

On certain Derivatives of Piperidine. By J. W. Brühl.*

The researches of Cahours have shown that piperidine is a secondary monamine, *i.e.*, that it requires the fixation of two methyl-, amyl-, &c., atoms to convert it into an ammonium base: hence the action of ethylene dibromide, according to the analogies observed by Hofmann, might be expected to give rise to either of the four bodies:—

Vinyl-piperidine.	Bromethyl-piperidine.	Oxethyl-piperidine.	Ethylene-dipiperidyl-diamine.
$\left.\begin{matrix}C_5H_{10}\\C_2H_3\end{matrix}\right\}N.$	$\left.\begin{matrix}C_5H_{10}\\C_2H_4Br\end{matrix}\right\}N.$	$\left.\begin{matrix}C_5H_{10}\\C_2H_5O\end{matrix}\right\}N.$	$\left.\begin{matrix}(C_5H_{10})_2\\C_2H_4\end{matrix}\right\}N_2.$

Of these the last appears to be principally produced.

On mixing 20 parts piperidine and 22 of ethyline dibromide, much heat is evolved, the temperature rising to 200°; the product is a nearly white solid mass, readily soluble in cold or hot water; from the aqueous solution alcohol precipitates small shining crystals, which may be purified by recrystallisation from boiling alcohol and washing with cold alcohol and ether, in which the product is practically insoluble; the pure substance gives numbers agreeing with the formula

$$(C_5H_{10})_2(C_2H_4)N_2.2HBr.$$

From the hydrobromide dissolved in water, caustic potash precipitates the base; this is a clear oily liquid, which boils at 263°, and has

* Deut. Chem. Ges. Ber., iv, 738.

powerful basic properties: in a freezing mixture it solidifies to a crystalline mass that melts at + 4°.

The nitrate, sulphate, oxalate, and hydrochloride, also the gold and platinum salts have been prepared; all are crystalline; the platinum salt is $\{(C_5H_{10})_2(C_2H_4)N_2.2HCl\}PtCl_4$.

By the further action of ethylene dibromide on ethylene-dipiperidyldiamine, there is produced, without disengagement of heat, the corresponding compound, $\{(C_5H_{10})_2(C_2H_4)_2.N_2\}Br_2$ = *diethylene-dipiperidyldiammonium bromide;* this, like the preceding, is soluble in water, and may be purified by precipitation by alcohol: treated with silver oxide, it, apparently, forms the corresponding di-hydroxyl compound $\{(C_5H_{10})_2(C_2H_4)_2N_2\}(OH)_2$, which on distillation splits up, forming the mono-ethylene base; possibly acetic aldehyde and crotonic aldehyde are simultaneously formed from this diammonium hydrate.

C. R. A. W.

On the Alkaloïds of Opium. By O. Hesse.*

In order to obtain the rarer alkaloïds, the black mother-liquors were taken (as obtained in the Robertson-Gregory process) from which the hydrochlorides of morphine, codeine, and pseudomorphine, had been separated. This liquor was first treated with an equal volume of water and precipitated with excess of ammonia; the clear liquor was exhausted with ether, and this again treated in the manner described in the Ann. Ch. Pharm. cliii, 47. The alkaloïds thus obtained can be now separated into two parts, the one part insoluble, and the other soluble in excess of sodium hydrate. The alkaline solution treated according to a former method, deposits first a small quantity of lanthopine, the filtrate from which contains neither codeine nor meconidine, for it is not coloured on warming with sulphuric acid; from it the author has obtained a small quantity of codamine. The solution is precipitated with ammonia, and the hard precipitate dissolved in a very small quantity of boiling dilute alcohol. White crystals are thereby obtained, from which the laudanine is separated by the action of hydriodic acid, with which it forms a difficultly soluble compound. *Laudanine* has the composition $C_{20}H_{25}NO_4$, instead of the formula $C_{20}H_{25}NO_3$, as formerly given; its melting point is 166°. *Codamine* is found to melt at 126°, instead of 121°, and has probably the composition $C_{20}H_{23}NO_4$.

The portion insoluble in sodic hydrate, which must contain the thebaine and papaverine, is dissolved in acetic acid, and the solution is neutralized in presence of alcohol, whereupon a crystalline precipitate is formed, consisting of papaverine and narcotine, which can be sepa-

* Deut. Chem. Ges. Ber., iv, 693.

rated by oxalic acid. The melting point of *narcotine* is given by the author as 176°, instead of 170°.

Papaverine, $C_{21}H_{21}NO_4$, when absolutely pure, dissolves in small quantities of sulphuric acid without coloration; generally, however, on warming a crystal of papaverine with concentrated sulphuric acid, a dark blue colour is produced, but when other crystals are added the colour is not increased; on the addition of water, papaverine sulphate is precipitated, as a resinous mass, which after a short time solidifies. No other alkaloïd of opium gives this reaction; pseudomorphine, which is the only one that is precipitated from its sulphuric acid solution by water, is obtained as a crystalline powder, not a resinous precipitate. Dilute nitric acid converts papaverine readily into nitropapaverine, $C_{21}H_{20}(NO_2)NO_4 + H_2O$, which occurs in colourless thin prisms, melting at 163°, and becoming yellow on exposure to light. When chloride of zinc and impure papaverine hydrochloride are allowed to act together for a short time, the impurities are decomposed, and a hydrochloride of an alkaloïd is obtained, which agrees in properties with pure papaverine hydrochloride. The new alkaloïd forms with acids very handsome crystalline salts, resembling the salts of cryptopine.

The neutralized acetic acid solution, from which the narcotine and papaverine have been separated, contains *thebaine*, which can be separated as the bitartrate by adding powdered tartaric acid. Instead, however, of tartaric acid, concentrated hydrochloric acid is added, which keeps the thebaine in solution, whereupon crystals of cryptopine hydrochloride are formed. From the dark-coloured liquid still remaining the author has been able to separate three other alkaloïds, protopine, laudanosine, and hydrocotarnine, by processes which will be described in another memoir.

Cryptopine, $C_{21}H_{23}NO_5$, melts at 217°, dissolves easily in chloroform, with difficulty in alcohol, and is insoluble in ether. It is strongly basic, and forms salts which can be obtained in crystals; with hydrochloric acid it forms two salts $C_{21}H_{23}NO_5.HCl + 6H_2O$, and with $5H_2O$, but the author has not obtained the salt with 2HCl, as found by T. and H. Smith. It is precipitated from cold neutral solution by hydrochloric acid as a gelatinous mass, but from hot solutions prisms are deposited.

Protopine, $C_{20}H_{19}NO_5$, may be separated easily from the former alkaloïd; it forms solid prisms with hydrochloric acid. It melts at 202°, and is somewhat difficultly soluble in alcohol and insoluble in ether.

Laudanosine, $C_{21}H_{27}NO_4$, dissolves sparingly in cold, but easily in hot benzol; it forms colourless prisms which melt at 89°. It is easily soluble in alcohol and ether, and has a basic reaction; with hydriodic acid it forms a very difficultly soluble salt.

Hydrocotarnine, $C_{12}H_{15}NO_3$, crystallises in large colourless prisms,

with $\frac{1}{2}H_2O$ as water of crystallisation; they melt at 50°, and give up the $\frac{1}{2}$-atom water. It volatilizes at 100° with partial decomposition, it dissolves easily in ether and alcohol; behaves like narcotine with concentrated sulphuric acid. Its reaction is basic, and it neutralizes dilute acids, forming salts which are easily soluble in water.

The author appends a valuable table, giving the colorations observed when the various alkaloïds are dissolved in pure strong sulphuric acid, and in acid containing traces of iron.

	Dissolves in pure acid.		In acid containing oxide of iron.	
	At 20°.	At 150°.	At 20°.	At 150°.
Codeine	Colourless	Dirty green	Blue	Dirty green.
Codamine	Colourless	Dirty red violet	Intense green blue	Deep violet.
Laudanine	Very faint rose-red	Deep red violet	Brown red, similar to cobaltic nitrate solution	At first green, then deep violet.
Laudanosine	Faint rose-red, somewhat stronger than laudanine	Ditto	Ditto	Ditto.
Cryptopine	At first yellow, then violet, and finally deep violet	Dirty green	Deep violet	Dirty green.
Protopine	At first yellow, then red, and finally bluish-red	Dirty greenish brown	Ditto	Dirty greenish brown.

A. P.

On the Betaine of the Phosphorus Series. By ARTHUR H. MEYER.*

BY the action of triethylphosphine on chloracetic acid, and of silver hydrate on the product of this action, Hofmann† has obtained a body which appears to be tri-ethylated glycocine, having the N replaced by P; similarly tri-ethylated glycocine itself is obtainable from tri-ethylamine, and tri-methylated glycocine from tri-methylamine; this last product is identical with the *oxyneurine* of Liebreich,‡ and the *betaine* of Scheibler§ (from *Beta vulgaris*). The author finds that trimethylphosphine (from phosphonium iodide and methyl alcohol) undergoes a similar reaction.

Equivalent quantities of trimethylphosphine and chloracetic acid (1 molecule of each) heated to 100° in a sealed tube for 5 or 6 hours

* Deut. Chem. Ges. Ber., iv, 734.
† Proc. Roy. Soc., xi, 525.
‡ Deut. Chem. Ges. Ber., ii, 13 and 167.
§ Zeit. f. Chem., ix, 279.

from a compound precisely analogous to that produced with triethylphosphine, and having the composition $(CH_3)_3(C_2H_3O_2)P.Cl$; this combines with platinic chloride, forming a platinum salt $(C_5H_{11}PO_2 . HCl)_2PtCl_4$, and by treatment with sulphuric acid furnishes a sulphate from which the free base is obtainable by treating it with baryta water, and the filtrate with carbonic acid. This base gives crystalline salts with hydriodic and nitric acids, the former of which was analysed; the base itself is a very hygroscopic crystalline mass, destitute of reaction on vegetable colouring matters; though it was not analysed, the author believes it to be *trimethylated phosphoglycocine, i.e.*, the *betaine of the phosphorus series* $= C_2H_2(CH_3)_3PO_2$. C. R. A. W.

Production of Urea by the Decomposition of Aqueous Hydrocyanic Acid. By G. Campani.*

A quantity of aqueous hydrocyanic acid having been left in a glass cylinder merely covered with a funnel and a glass plate, till the liquid had evaporated, a solid residue was found at the bottom, consisting partly of brown amorphous matter, partly of yellowish crystals, which in form, taste, reaction with mercuric nitrate, mercuric chloride and potash, &c., exhibited all the characters of urea. This result confirms the observation formerly made by the author (*Nuovo Cimento*, t. 18) respecting the portion soluble in water, of the product obtained by the gradual decomposition of aqueous hydrocyanic acid. H. W.

Nigella Seeds or Black Cummin. By F. A. Flückiger.†

The seeds of *Nigella sativa*, a ranunculaceous plant growing on the Mediterranean coasts, in Egypt, Trans-Caucasia, and India, were found by Reinsch in 1841 to yield 35·8 per cent. of fat oil, 0·8 per cent. of volatile oil, and only 0·6 per cent. of ash. He gave the name of *Nigellin* to a bitter extract resembling turpentine, yet soluble in water as well as in alcohol, though not in ether.

By submitting 25 lb. of fresh seed to distillation, Flückiger has obtained a nearly colourless essential oil in even smaller quantity than Reinsch. It has a slight odour, somewhat resembling that of parsley oil, with a magnificent bluish fluorescence, as already remarked by Reinsch.

In a column 50 mm. long, this oil deviates the ray of polarized light 9·8° to the left. Its specific gravity is 0·8969. The chief part of it, when distilled with chloride of calcium in a current of dry carbonic acid, comes over at 256°. In an elementary analysis it yielded —carbon 83·3, and hydrogen 11·8 per cent., corresponding to the formula $2C_{10}H_{16}.H_2O$.

* Gazzetta chimica Italiana, i, 472. † Pharm. J. Trans. [2], ii, 161.

The residual portion was almost entirely devoid of rotatory power; it yielded carbon—87·89, and hydrogen 11·72 per cent., after having been rectified by means of sodium. This part of the oil consequently belongs to the terebenes $C_{10}H_{16}$.

The fat oil extracted by means of boiling ether, from seed grown in Germany, previously finely powdered (necessarily including some essential oil which imparted to the other its fluorescence) amounted to 25·6 per cent. It is a fluid fat which does not congeal at 15°; it was found to consist chiefly of olein, besides which it yielded a considerable amount of a solid fatty acid, the crystals of which, after reiterated purification, melted at 55°. The melting point did not rise by re-crystallisation, the acid being probably a mixture of palmitic and myristic acids.

Nigella seeds, powdered and dried over sulphuric acid, yielded 3·3195 per cent. of nitrogen, answering to about 21½ per cent. of albuminous matter.

It is stated in the Pharmacopœia of India, that Nigella seeds are carminative, and they were formerly so regarded in Europe. In the East generally they are used as a condiment to food, and in Greece, Turkey, and Egypt, they are frequently strewed over the surface of bread and cakes in the same manner as anise or sesame. The fixed oil of the seeds is also expressed for use.

The Purgative Principles of Alexandrian Senna. By BOURGOIN and BOUCHAT.*

THE results obtained by different chemists with respect to this drug being very contradictory, the authors have subjected it to a further examination, from which they infer that senna cannot be classed with the plants possessing but a single purgative principle, and that no single one of the constituent principles of the plant, taken by itself, can pretend to represent the whole of its general properties. In other words, besides chrysophanic acid, which exists in small quantity only, senna contains at least two other purgative principles: one represented by cathartic acid, the other contained in the cathartine of Lassaigne and Feneulle. The authors have satisfied themselves, that cathartine does not contain a trace of cathartic acid.

The best preparation of senna is the aqueous infusion, with or without the mucilaginous matter,—such as that described in the memoir under the name of liquid extract, which is obtained by mixing the aqueous infusion with alcohol to precipitate mucilaginous matter, and evaporating at a gentle heat till a liquid remains equal in weight to the leaves originally used.

* Pharm. J. Trans. [2], ii, 223.

The liquid so obtained is of a dark brownish-yellow colour, and has a bitter, slightly nauseous flavour. It gives no precipitate with water or proof-spirit, but with absolute alcohol it yields an abundant blackish precipitate, containing the cathartic acid of Dragendorff and Kubly.

Physiological Chemistry.

On Proteids. By H. Hlasiwetz and I. Habermann.*

Notwithstanding the great advances in chemistry of late years, and specially in the synthesis of organic compounds, little is as yet known regarding the constitution of protein substances. The authors, however, see numerous indications which point to the carbohydrates as playing an important part in the formation of these substances. Both groups, the carbohydrates and the proteids, include a host of isomeric and polymeric substances, some soluble and unorganised, as dextrin, albubin, &c., others insoluble and organised, as cellulose, animal cellular tissue, keratin, &c. The insoluble seem to be derived from the soluble by molecular condensation. Intermediate between the two forms seems protoplasm. Numerous parallels can be drawn between the carbohydrates and the proteids. The mucus-like carbohydrates resemble animal mucus. Dried albumin, dried soluble fibrin, and casein resemble gum and dextrin. The protoplasm of plants corresponds to the granulose of animals, cellulose to animal cellular tissue, hardened cellulose to keratin, &c.

In both groups are substances which swell up in water without undergoing solution. Some gums, like proteids, require the presence of alkaline bases for their solution. The passing from the soluble to the insoluble form and *vice versâ*, is seen in both.

The substances of both groups undergo fermentation, and the chief products of fermentation stand in a manifest and simple relation to each other. Only for tyrosine is there no corresponding non-nitrogenous fermentation-product of the carbohydrates.

These and many other facts render it probable that the proteids and carbohydrates stand in a genetic relation to each other. With a view to determine more definitely the nature of this relation, the experiments of which the results are here detailed, were undertaken. The method employed was to dissolve and decompose the proteids (animal and vegetable albumin, casein and fibrin) by means of bromine and water. To this end, given quantities of the substances corresponding to 50 grams dry substance were introduced into a champagne bottle, together with $\frac{1}{2}$ litre of water and 50 grams bromine. The bottle was

* Ann. Chem. Pharm., clix, 304—333.

securely closed by means of a cork, through which passed a small tube, the free end of which was hermetically sealed. The bottle was placed in a water-bath, kept at a constant level and constant heat. When the first quantity of bromine had disappeared, the cooled bottle was freed from vapour by opening the closed end of the tube, fresh bromine was added, the tube closed, and the bottle again placed in the same condition as before.

Among the gases which were evolved when the bottle was opened, the chief was carbonic acid. In all cases there remained an insoluble residue no longer capable of being acted on by bromine (A). This substance is brown, often flocculent, but mostly of pasty consistence. In the former case it exhibits the characters of *humus*, and is only partially soluble in alcohol. What remains insoluble in alcohol is soluble in alkaline liquids—again precipitable by acids. It is non-nitrogenous. If it is pasty, a great portion is soluble in alcohol, leaving numerous small glistening crystals. These, when purified by sublimation, form golden yellow glistening scales having all the characters of *bromanil*. The alcoholic solution leaves on evaporation a resinous mass. When this was boiled in a flask with faintly alkaline water, a part sublimed and formed crystals. These contained both bromine and nitrogen. When dissolved in hot alcohol they formed on cooling a meshwork of silky crystals. They agreed in properties with *tribromamido-benzoic acid*. The residue in the flask, after cooling and addition of dilute sulphuric acid, gave a small quantity of a pitch-like substance. The acidified liquid yielded to ether a rancid-smelling, thickish, yellowish acid, which contained a little bromine. This acid appeared to be *caproic acid*. It results from the decomposition of leucine.

The contents of the bottle freed from the insoluble residue, A, were distilled. The distillate in all cases consisted of water containing acid and a heavier, more or less marked layer of a fluid coloured brown by free bromine. At the same time, traces of a bromininated substance crystallised on the cool part of the tube (B *a* and *b*). The bromine was separated from the liquid by washing with dilute caustic potash. This substance proved to be *bromoform*. The sublimate resembled *bromobenzoic acid*.

The liquid which remained in the retort after the distillation of B, was filtered. The filtrate was exhausted with ether, and gave, after evaporation of the ether, a yellowish or brownish, intensely pungent, oily liquid, which always contained a greater or smaller quantity of crystals consisting of *oxalic acid*. The oily liquid (C) was miscible with alcohol and water, and had a very strong acid reaction. It appeared to be a mixture of *mono-* and *dibromoacetic* acids.

The liquid which remained after extraction with ether was freed from bromine by silver-oxide, and gave, on addition of neutral

acetate of lead, a copious precipitate containing oxalic acid, a little phosphoric acid, and some colouring matter (E).

The filtrate from the precipitate gave, with basic acetate of lead, a more copious precipitate (F). Freed from lead, it formed a peculiar gelatinous substance, having an intensely acid reaction. Dissolved and treated with baryta, it gave a precipitate of sulphate and phosphate of baryta. The filtrate gave with basic lead-acetate a lead salt which, when freed from lead, left an acid which formed blue crystals with cupric oxide. The acid was *aspartic acid*. Probably also there was some *melamic acid*. *Glutamic acid* was never found.

The liquid (G) which remained after the separation of E and F, when freed from lead and evaporated to the consistence of a syrup, formed a powdery, whitish deposit on the sides of the vessel (H). This substance was soluble in boiling water and dilute alcohol, from which it crystallised in scales. It was found to be *leucine*.

The syrupy substance, after the separation of H, when treated with alcohol, was partly dissolved (I); the rest was converted into a friable mass (K).

The alcoholic solution on evaporation deposited fine crystals which had the characters of *leucimide*.

The friable mass resembled the soluble modification of proteids or *peptones*.

In no case was *tyrosine* found, but bromanil and tribromoamidobenzoic acid are in all likelihood the products of its decomposition by bromine.

The decomposition-products of the proteids can all be ranged under the fatty and aromatic series. The highest members of the groups are leucine, aspartic acid, glutamic acid, and tyrosine; all the others are derivates from these.

Urea and uric acid have not yet been produced, but the authors hope by future experiments to throw light on these substances also.

D. F.

Gelatiniform Matter, Albuminose, Exalbumin, Galactin. By M. Morin.* *

The author asserts that the substances described as albuminose and exalbumin respectively, are identical with the gelatiniform substances discovered by him in 1842. He now proposes to term it galactin, because milk forms its most abundant source. From this liquid, galactin is prepared by first precipitating the casein with acetic acid, coagulating the albumin by boiling, removing fat by ether, concentration, filtration from earthy phosphates, allowing the sugar to crystallise out, and, finally, precipitating the galactin by alcohol. As thus pre-

* J. Pharm. [4], xiv, 11—20.

pared, it contains a little gelatin. 35 parts of dried milk yielded about 1 part of galactin.

Galactin is soluble in water, insoluble in ether and in alcohol, and is not transformed into gelatin by boiling its aqueous solution. It is precipitated by tannin, but the precipitate differs from the corresponding precipitate with gelatin in redissolving at a temperature of 60°. This property renders the detection of galactin in morbid fluids easy.

Galactin is an azotized substance; it emulsifies fats, and is found normally in the blood, the gastric juice, the membranes, the fluid of the fœtal cotyledons, milk, and eggs; also in many morbid fluids. Moreover, as it exists in notable quantity in the juices of edible plants, galactin probably plays an important part in the nutritive processes of the animal economy. The paper contains some physiological speculations relative to this and other questions. T. S.

Utilisation of certain Inorganic Constituents in the Animal Body. By K. Voit.*

The importance of certain inorganic substances for nutrition was first recognised by Liebig, and confirmed by Forster, who showed by experiment, that if an animal was supplied with food from which the inorganic constituents were absent, although all the other necessary ingredients were present, it died almost as quickly as one which had been deprived of food altogether. Liebig believed that in order to sustain life, all the inorganic constituents necessary for the construction of the body must be present in the food ready formed and in sufficient quantity. Forster found that an animal may live a long time on food which does not contain salts in sufficient quantity for the processes which take place in the body, as the amount absorbed from the intestine may be supplemented by salts which are liberated by the decomposition of organic substances in the body and are used over again. In the present paper, Voit shows that it is not necessary for the food to contain an ash whose composition corresponds exactly with the requirements of the blood or organs, and that the most manifold processes of compensation may occur in the organism. Besides the inorganic materials necessary for the body, others which are unnecessary may be present in the food, and may enter the blood, but the organs possess the power of selecting those which are needful, and the others are excreted. Several examples of this are given by the author.

There are some substances, such as muscle, yolk of egg, wheat, &c., whose ash contains more phosphoric acid than is necessary to form bibasic salts with its alkali and alkaline earths; others again, such as blood, milk, white of egg, and peas, contain alkali in excess.

* Wien. Acad. Ber., lxii; N. Repert. Pharm., xx, 422—432.

It might be supposed that no free alkali could be produced in the body from food whose ash contained free phosphoric acid, and that, therefore such articles of food, as wheat, yolk of egg, and muscle, could not of themselves nourish the body in which free alkali is present in the blood and juices.

This supposition would also seem to be confirmed by experiment. Chossat found that pigeons fed upon grain alone, soon became unwell, and died after eight or ten months from diarrhœa. Magendie observed, that dogs fed on the yolk of eggs alone, refused them entirely on the fourth day, and that dogs fed on the yolk and whites lived long, but became thin and weak. The result in these cases might be due, however, to insufficient quantity, and not imperfect quality; and Voit fed pigeons, whose brain had been removed, on nothing but wheat and hardwater, for nearly two years, without their nutrition being impaired, and kept pigeons alive, without loss of weight, and with the alkalinity of the blood unchanged, for weeks on the yolk of egg alone. Dogs can also be nourished perfectly for years on meat alone or meat and fat.

These experiments show that the animal body may be sustained by articles of food which leave an ash containing excess of phosphoric acid, and therefore, the blood and fluids must have the power of retaining firmly their excess of alkali and also of supplementing it from acid salts of alkalis, the excess of acid being excreted.

Voit tried to imitate this by adding a little dilute phosphoric acid to strongly alkaline albumin, and then dialysing it, but was unable to find free acid in the first diffusate. The separation of acid from the alkaline blood is further shown by the acidity of the urine after taking dilute sulphuric acid; by the continued alkalinity of the blood, and the presence of free phosphoric acid in the urine of swine fed on bran which leaves an acid ash; and by the fact that acids do not take alkali with them from the blood when they are excreted, which appears from Wöhler's observation, that vegetable acids taken into the intestine are excreted as such in the urine, while their alkaline salts are excreted as carbonates; and also from the circumstance that the acidity of the urinary ash corresponds with that of the food eaten, being alkaline when the animal has been fed on meat or peas, and acid when on yolk of egg. In the embryo the excretion of phosphoric acid is impossible, and yet organs are formed. It had been supposed that the phosphoric acid in the yolk was neutralised by lime from the shell; but Ernest Hermann, under Voit's direction, found that neither the weight nor the amount of inorganic substances in the shell was altered during incubation. The alkali for the blood of the chick is derived from the white of the egg, which contains so much alkali that the ash of the whole egg is alkaline, although that of the yolk alone is acid. T. L. B.

Manganese in the Blood. By G. CAMPANI.*

THE author finds that manganese exists in ox-blood, in the corpuscles as well as in the serum, both of which also contain iron; and that on examining equal weights of the ash of the corpuscles and of the portion of the serum-ash which is insoluble in water, both manganese and iron are found to exist more copiously in the ash of the corpuscles than in that of the serum. The portion of the serum-ash which is soluble in water contains traces of iron but no manganese.

H. W.

Assimilation of Meadow-hay by Sheep. By MÄRCKER.†

THE author made numerous experiments with two samples of meadow-hay, and two experiments with hay of the second cutting. He found that, for 100 of the various constituents consumed, the following proportions were digested:—

	Hay I.	Hay II.	Hay 2nd cutting.
Total organic matter	60·2	61·9	70·2
Albuminous compounds	54·7	54·4	68·3
Crude fibre	60·6	57·4	68·2
Non-nitrogenous extractive matter	61·7	68·0	74·2

The portion of the fibre digested was the cellulose. The author added gluten, starch, bean-meal, and bean-meal and starch to the hay, to ascertain whether alteration of its composition had any influence on its digestibility. Gluten had no effect. Starch reduced the proportion of albumin digested. When starch was used, much passed undigested. When bean-meal was added to the starch, all the starch was digested.

The nitrogen in the excreta was found to equal the nitrogen consumed in food, unless albumin was assimilated. No nitrogen was lost. An increase of albumin in food does not necessarily determine a greater assimilation of albumin. An increase of the non-nitrogenous part of food does increase the proportion of albumin assimilated.

R. W.

Assimilation of Clover-hay, and Mangolds by Sheep. By E. WOLFF.‡

THE author first fed two sheep with hay made from red clover; he then fed the same sheep with clover-hay, and mangolds. Having ascertained in the first experiment what proportion of the different

* Gazzetta chimica Italiana, i, 469. † Versuchs Stationen Organ, xiii, 16—24.
‡ Versuchs Stationen Organ, xiii, 21—23.

ingredients of the hay was digested, he assumes that the same proportion of the hay was digested during the second diet, and then finds by calculation, what proportion of the constituents of the beet-root had been digested. The composition of the foods used, and the mean proportion of the various constituents digested, were as follows:—

Constituents of Food.	Red Clover Hay.		Mangold Wurzel.	
	Composition per cent.	Digested for 100 of each constituent supplied.	Composition per cent.	Digested for 100 of each constituent supplied.
Water	17·51	—	89·17	—
Ash	6·96	40·4	·92	86·5
Fatty matter	3·17	54·9	·06	—
Crude fibre	20·09	52·0	·76	40·6*
Protein compounds	16·00	58·9	1·47	76·1
Non-nitrogenous extractive matter	36·27	63·3	7·62	97·2
Total organic matter.	75·33	59·3	9·91	89·2

The author found clover to be more digestible when young than when in full bloom.

R. W.

Physiological Action of Tobacco when used as a Narcotic, with especial reference to the Constituents of Tobacco Smoke. By H. Vohl and H. Eulenberg.†

The authors first give a short account of the introduction of tobacco and a summary of its chemical history, from which they conclude that the action of tobacco, when used as a narcotic, has been erroneously attributed to the nicotine it contains. This conclusion they confirm by analyses and experiments of their own.

The amount of nicotine in snuff they found to be only from ·0392 to ·062 per cent.; in the strongest tobacco for chewing there was only a mere trace of nicotine, and in other specimens of the same kind there was none at all, so that nothing like nicotine-poisoning can result from the use of these sorts.

They then analysed the smoke of strong tobacco containing 4 per cent. of nicotine, burning part of it in a pipe and part of it as cigars. The smoke was drawn by an aspirator first through potash-solution to

* The figures from which this mean is calculated are very discordant.—R. W.

† Arch. Pharm. [2] cxlvii, 130—166.

collect acids, and then through dilute sulphuric acid to collect bases. Besides this, the gases given off when cigars were smoked were collected and examined. These consisted of oxygen, nitrogen, carbonic oxide, and marsh-gas.

The potash-solution soon became brown, acquired an almost unbearable odour of tobacco-juice, and an oily substance collected on the surface which became of a consistence like butter when cold. This oily substance was removed, washed with water and dilute sulphuric acid, and distilled. It began to boil at 200°, but the boiling point was not constant, and gradually rose. The distillate was at first fluid and oily, but when the temperature rose to 300°, the substance which then passed over thickened on cooling to a laminated mass, which, after being several times recrystallised from ether, formed pearly-white scales, melting between 94° and 95°, and having a higher boiling point than mercury. In these characters, as well as in their percentage-composition, they agree with the carbohydrate ($C_{19}H_{18}$) discovered by Knauss and examined by Fehling and Fritsche. The oily distillate, after repeated treatment with potash and sulphuric acid, was colourless, neutral, burned with a smoky flame, and had a specific gravity of 0·8 to 0·87. From its percentage composition (92 and 93 C., and 8 or 7 per cent. H.) it seems to be a mixture of different hydrocarbons belonging to the benzene series or a series analogous to it. None of the nitro-compounds obtained by treating it with nitric acid had any definite character, and when they were deoxidised, no trace of aniline was found, showing that benzene was absent. After separating the oily substance, the potash-solution was distilled, and the distillate added to the sulphuric acid through which the smoke had already been passed. On saturating the residue with excess of dilute sulphuric acid, keeping it well cooled, a large amount of gas was given off which consisted of carbon dioxide, hydrogen cyanide, and hydrogen sulphide. The two latter gases were also detected directly in the potash-solution. When it had been used for absorption during a considerable time, the reaction of cyanogen disappeared, and that of sulphocyanogen took its place. This may be the reason of a recent statement that tobacco smoke contains no cyanogen.

The acid potash-solution was distilled, and acetic, formic, propionic, butyric, valerianic, and carbolic acids and creasote were discovered in the distillate; caproic, caprylic, and succinic acids were doubtfully present.

The sulphuric acid which had served to absorb the bases had become dark brown and thick, and a dark-brown resin had separated. The liquid was filtered, and, after addition of the distillate from the potash, partially evaporated, cooled, and saturated with caustic potash, whereupon ammoniacal vapours escaped, and a brown oil, with an odour of tobacco-juice, collected on the surface. The liquid was distilled and

saturated with caustic potash, redistilled, and the most volatile bases were collected in a Horsford's nitrogen-apparatus containing dilute hydrochloric acid. These were found to be ammonium chloride and traces of ethylamine. The distillate was neutralised with dilute sulphuric acid, filtered, evaporated, and treated with strong potash, the bases taken up by ether, and the ethereal solution distilled. The distillate contained only ammonia. The oily residue was dried by caustic potash and submitted to fractional distillation. The resulting bodies were further separated by repeated distillation and crystallisation of their platinum-salts, and at last the whole series of picoline or pyridine bases, analogous to the aniline bases, were obtained.

The identity of the following bases was determined by the boiling point, percentage-composition, and the composition of the platinum double salt. *Pyridine*, C_5H_5N, boiling point 115°—116°. *Picoline*, C_6H_7N, boiling point 134°—135° C. *Lutidine*, C_7H_9N, boiling point 155°. *Collidine*, $C_8H_{11}N$, boiling point 171·5°, is isomeric with xylidine, and is identified by the authors with the aldehydin of Ador and Baeyer by its composition and characters. *Parvoline*, $C_9H_{13}N$, boiling point 187°—188°, isomeric with cumidine. *Coridine*, $C_{10}H_{15}N$, boiling point 211°. *Rubidine*, $C_{11}H_{17}N$, boiling point 230°, and, probably, *Viridine*, $C_{12}H_{19}N$, boiling point 251°, were obtained in too small quantities to determine their percentage-composition, and were identified by their boiling points and platinum salts. Nicotine was carefully looked for, but no trace of it was found, and the authors thus fully confirm the observations made by Zeise in 1843, that it does not exist in tobacco-smoke. They find that it can be easily separated from the pyridine bases, as it forms with zinc chloride a double salt difficultly soluble in alcohol, which the pyridine bases do not. The formula of this salt is $C_{10}H_{14}N2HClZnCl_2 + 8H_2O$. The fact that stronger tobacco can be smoked in cigars than in a pipe is explained by the greater proportion of volatile bases present in the smoke of a pipe, and especially by the large quantity of very volatile and stupefying pyridine, while in a cigar little pyridine and much collidine is formed.

The authors think that the disagreeable symptoms which are felt by persons beginning to smoke, and the chronic affections which occur in those who smoke to excess, as well as the cases of poisoning from swallowing tobacco-juice, are due, not to nicotine, but to the pyridine and picoline bases. The idea that they were due to nicotine originated in the fact that picoline bases having a high boiling point, such as parvoline, resemble that alkaloïd greatly both in smell and in physiological action.

The authors did not test the physiological action of each base separately, but only that of a mixture of those bases which volatilise under 160°, and of those between 160° and 250°.

Both of these produced, like nicotine, contraction of the pupil, difficulty of breathing, general convulsions, and death. On post-mortem examination the respiratory passages and lungs were found congested. They act more quickly when taken internally than when injected subcutaneously, but they do not act so quickly as nicotine.

Plants which contain no narcotic are not unfrequently used for smoking, instead of tobacco. The authors tested the action of the pyridine bases produced from dandelion, willow-wood, stramonium, and of pure picoline from Boghead coal. These had an action very much resembling, though weaker than, that of the bases from tobacco; but with the exception of those from willow-wood, they produced no contraction of the pupil. The vapour of picoline was also tested and found to be poisonous, producing great irritation of the respiratory passages, slight convulsions, and death.

The authors are acquainted with a person who can swallow the juice from a tobacco-pipe without being affected by it, but they consider that this exception does not impair the rule that picoline bases have a powerful action on the organism. They also think that the action of opium, when smoked, is not due to the alkaloïds it naturally contains, and that the difference of its action from that of tobacco is simply due to a difference in the bases which are produced when the two substances are smoked.

T. L. B.

Relations of the Spectral Properties of the Elements to their Physiological Properties. By F. Papillon.*

It is known that among the diatomic and tetratomic metalloïds, the lines observed in their several spectra approach nearer to the violet in proportion as the atomic weights increase, whilst among the metals an inverse relation is observed. It has also been found that the toxic qualities of the metals increase directly as their atomic weights. It is asserted in this memoir that the converse obtains with the monatomic metalloïds—that their physiological activities are in the inverse ratios of their atomic weights. The triatomic metalloïds, however, follow the same law as the metals.

T. S.

The Toxicology of the Benzene Group, of Nitroglycerin, of Nitric Acid and of Sulphuric Acid. By W. Starkow.†

This paper is one mainly of physiological interest, and is intended to establish: (1.) that the replacement of H by the radical NO_2 in the hydrocarbons alters the nature of their action and increases their

* Compt. rend., lxxiii, 791—2. † N. Repert. Pharm., xx, 489—492.

toxicological properties, if they are only correspondingly soluble. Various changes in the spectroscopic appearances of the poisoned blood are described. (2.) The action of aniline on blood is similar to that of ammonia and phosphine. (3.) Dinitrobenzene, $C_6H_4(NO_2)_2$, is remarkable on account of its highly poisonous nature and sparing solubility. (4.) Nitroglycerin is analogous to nitrobenzene in its chemical effects on the blood-pigment. (5.) Nitric and sulphuric acids, but not hydrochloric and phosphoric acids, cause alterations in the blood similar to those produced by nitro-compounds (production of the spectroscopic bands of acid hæmatin, &c.) : hence these acids act generally as well as locally. (6.) Some organic nitro-compounds, as, for instance, nitroglycerin, owe their poisonous nature to the substitution of the radical of nitric acid for hydrogen. (7.) Letheby's view that nitrobenzene is changed in the organism into aniline is doubtful. (8.) Chlorobenzene, C_6H_5Cl, is a better reagent than ether for the production of blood-crystals. T. S.

Comparative Influence of various Substances in Preventing the Decomposition of Organic Bodies. By F. C. Calvert.*

A memoir devoted to a determination of the comparative power of various substances ordinarily used as antiseptics. For this purpose two series of experiments were made. The first consisted in placing in uncorked bottles solutions of albumin and flour paste, with various proportions of the antiseptics. The following were the results :—

Antiseptic employed.	Percentage of antiseptic.	Days in which offensive odour was developed at temp. of 22 —27°.	
		Albumin.	Flour paste.
Sulphites mixed with Light oils	5	11	15
Carbolic disinfecting powder	5	Remained sound	Remained sound
Zinc chloride	2	15	Remained sound
Chloride of lime	2	16	14
Potassic permanganate	3	14	6
Tar oil	2	11	25
Carbolic acid	2	Remained sound	Remained sound
Cresylic acid	2	Remained sound	Remained sound
Nothing	0	5	7

In the second series of experiments sound meat was suspended in bottles over the several antiseptics.

* J. Pharm. Chim. [4], xiii, 380—383.

Antiseptic used.	Became tainted.	Putrid.
Potassic permanganate	2 days.	4 days.
McDougall's disinfecting powder	12 ,,	19 ,,
Chloride of lime	14 ,,	21 ,,
Tar oil	16 ,,	25 ,,
Chloride of zinc	19 ,,	25 ,,
Carbolic disinfecting powder	Did not become tainted, but dried up and became quite hard.	
Carbolic acid		
Cresylic acid		

T. S.

Agricultural Chemistry.

Influence of Heat and Light upon the Evolution of Oxygen by Water-plants. By R. HEINRICH.*

THE author first treats of the effect of temperature. He experimented with single leaves of the *Hottonia palustris*. These were placed in common water, and exposed to the sunlight of a cloudless sky in the month of May. The temperature of the water was varied according to the nature of the experiment. The lowest temperature at which any separation of gas-bubbles was visible was 2·7°, but no regular evolution of bubbles from the leaf took place below 5·6°. The most active formation of gas-bubbles, reckoning by their number, was at a temperature of 31°. The evolution ceased altogether when the temperature exceeded 50°—56°, but the plant resumed its activity when placed in cooler water. If, however, the leaves were kept for ten minutes in water at 69°, their power of decomposing carbonic acid in sunlight was destroyed.

Cloëz and Gratiolet had observed that *Potamogeton* ceases to evolve oxygen when the temperature is lowered to 10°; on raising the temperature, evolution commenced at 15°. Sachs found that *Vallisneria spiralis* ceases to produce bubbles at 6°.

The author next describes results obtained with artificial light. Numerous experimenters had endeavoured to obtain an evolution of oxygen under the influence of artificial light: all had failed. The author had noticed that the sensibility of a plant to light depends much on the conditions in which it has been previously placed. A plant kept in moderate reflected light gives off gas readily in a slightly stronger light, whereas plants previously exposed to bright sunlight, or

* Versuchs Stationen Organ, xiii, 136—154.

kept in darkness, will fail to produce gas under this moderate illumination. The author made use of this fact in his experiments. He employed as his source of light three magnesium wires. After the first wire had burnt $3\frac{1}{2}$ minutes, the second wire was also ignited. When this had burnt $3\frac{1}{2}$ minutes, the third wire was added. There was thus a progressive increase in the intensity of the light. The leaves of the *Hottonia palustris* had previously been kept under various conditions as to light; all the leaves were however placed in darkness for two hours before the experiment, so that all formation of bubbles ceased. No gas was evolved during the combustion of the single wire. During the combustion of the second wire, evolution commenced on the leaves previously accustomed to the reflected light of a room; this evolution became well marked as the illumination increased, but ceased when two of the wires were extinguished. The leaves previously exposed to sunlight gave off a few bubbles towards the end of the experiment; those kept for two days in darkness evolved no gas. The experiment lasted 14 minutes.

Since these experiments, E. Prilleux has published results obtained with the electric light, the oxy-hydrogen lime light, and gas flames. He operated on branches of the *Elodea canadensis*, and obtained with each illumination some evolution of gas, but much less than in the author's experiments,—a difference which Heinrich considers as probably due to the absence of the precautions requisite to render the plant sensitive to light.

R. W.

Water-culture Experiments with Maize. By P. Wagner.*

I. *Experiments with Creatine.*—These experiments were made to complete the author's previous investigation in 1868. Three maize plants were transferred (on May 1) to a solution containing $\frac{1}{2000}$ its weight of the following mixture:—

$$KH_2PO_4 + \tfrac{1}{4}CaCl_2 + \tfrac{1}{4}MgSO_4 + xFe_2P_2O_8 + \tfrac{1}{2}C_4H_9N_3O_2Aq.$$

The experiment was conducted with the precautions usual in water-culture. The plants grew fairly well. After blooming in July, two of the plants were taken and examined for creatine: it was found distinctly in the body of the plant, but not in the root. The remaining plant was harvested on August 14; it had reached a height of 88 cm., and produced 22 seeds. Hampe had found that urea is absorbed by the plant in an unaltered state; it appears that creatine belongs to the same class of nitrogenous compounds.

* Versuchs Stationen Organ, xiii, 69—75, and 218—222.

II. *Experiments with Manganese Salts.*—Birner and Lucanus had experimented on the replacement of iron by manganese, but with negative results. The author tried both manganous and manganic salts. The solution contained, in the first case, $\frac{1}{1000}$ of the following mixture :—

$$KH_2PO_4 + \tfrac{1}{4}CaCl_2 + \tfrac{1}{4}MgSO_4 + NH_4NO_3 + \tfrac{1}{8}Mn_3P_2O_8.$$

In the second case an equivalent quantity of manganic phosphate was substituted. The maize-plants were placed in the solutions on May 3. The plants in the manganous solution, though carefully tended, became in a short time completely bleached, and died about the middle of June. One plant was removed on May 24 to a solution containing ferric phosphate and no manganese. This plant recovered its green colour to a considerable extent, but only reached a height of 23 cm., and died towards the end of June. The experiments with manganic salts had no better success. Some of the plants transferred to a solution containing $\frac{1}{10000}$ of potassium ferrocyanide, recovered to some extent their green colour (a fact previously observed by Knop), but only attained 23 cm., and did not bloom. The author concludes that manganese is incapable of replacing iron in its function of chlorophyll formation.

III. *Experiments with a Solution destitute of Chlorine.*—Nobbe, Siegert, and Leydhecker, observed that buckwheat, when grown in solutions free from chlorine, exhibits certain peculiar abnormal appearances, and remains unfruitful. Beyer, experimenting with oats and peas, found that the absence of chlorine prevented perfect development. Knop, on the other hand, states that buckwheat, maize, and other plants, grow well without chlorine, and concludes that this element is no part of the essential food of plants. The author placed four maize plants in May in a solution destitute of chlorine. Towards the end of the month they were all in a sickly condition, but on further acidifying the solution they revived. When harvested in August the plants had reached a height of 89—103 cm. Three of the plants produced a little seed, the most fruitful yielded 5 ripe seeds. The development of the plants was not perfect, and in some respects peculiar. The author proposes to continue the investigation.

R. W.

Composition and Nutritive Value of the Prickly Comfrey (Symphytum asperrimum). By A. VOELCKER.*

THE prickly comfrey, a native of the Caucasus, is at present cultivated in some parts of Ireland as food for dairy stock. The plant is

* Jour. Roy. Agri. Soc. [2], vii, 387—389.

perennial, is easily propagated by cuttings from the root, and yields a heavy crop. The ordinary produce is about 30 tons per acre, in several cuttings, but 82 tons has been reached. Analysis of plants grown in Oxfordshire gave the following results:—

	Natural state.	Dried at 100°.
Water	90·66	—
Oil and chlorophyll	·20	2·20
Soluble nitrogenous compounds	1·10	11·81
Insoluble nitrogenous compounds	1·62	17·31
Gum, mucilage, and a little sugar	1·28	13·65
Woody fibre	3·30	35·43
Soluble mineral matters	1·25	13·32
Insoluble mineral matters	·59	6·28
	100·00	100·00
Total nitrogen	·434	4·66

Judging from its composition, the plant will have about the same feeding value as green mustard, turnip-tops, or Italian rye-grass grown on irrigated land.

R. W.

Field Experiments on Root Crops. By A. Voelcker. (Journ. Roy. Agri. Soc. [2] vii, 365—387.)

Analytical Chemistry.

Use of Porous Hollow Cones as Filters. By C. E. Munroe.*

In cases where it is impracticable to ignite precipitates previous to weighing, but necessary that they should be dried above 100°, it is proposed to collect them on hollow cones made of light earthenware, and having an angle of about 60°.

The said filters should be washed with concentrated hydrochloric acid, subsequently with distilled water, then dried, weighed in a porcelain crucible, and used as follows:—An elastic ring is fixed to the upper rim of a glass funnel, the cone inserted, the liquid to be filtered added, and the tube of the funnel connected with a Bunsen's pump.

To test the method, antimonious sulphide was precipitated by sulphuretted hydrogen from weighed quantities of tartar emetic, and the precipitate was transferred to earthenware filters, washed, and dried at 300°. The first experiment gave Sb_2S_3, containing to 36·59 per cent. of Sb; the

* Ann. Ch. Pharm., cxlix, 274.

2nd, to 36·59; the 3rd, to 36·59; the 4th, to 36·55; the calculated value is 36·52.

Arsenic was also estimated as tersulphide with equally good results, five experiments giving as the mean 75·72 per cent. of As, the calculated value being 75·76.

A. T.

Detection of Iodine in the Form of Metallic Iodides. By G. CAMPANI.*

A NEW method of testing for iodine, published by Pelloggio, in 1870,† which consists in subjecting the liquid under examination to the action of an electric current, after addition of starch-paste and slight acidulation with sulphuric acid—has lately been applied by Campani to the detection of iodine in the urine of patients under treatment with potassium iodide.

The urine of an individual who had taken 0·230 grm. of potassium iodide two hours previously, gave by Pelloggio's method, distinct indications of iodine after a few seconds; and even when the urine was diluted with three times its bulk of water, the blue iodine coloration was very evident round the platinum wire forming the positive pole; but when the same urine was diluted with 15 vols. water, the coloration was not developed in the slightest degree, although the passage of the current was continued for two hours. In this same diluted urine, however, the presence of iodine was manifested faintly by starch and bromine-water, and more plainly with bromine-water and carbon bisulphide.

From this and other experiments leading to similar results, Campani concludes that Pelloggio's method is inferior in delicacy, at least in testing for iodine in urine, to the method with bromine-water and starch or bisulphide of carbon.

H. W.

Improvements in Chlorimetry. By J. SMYTH.‡

THE use of the milky solution of bleaching powder in chlorimetry being unsatisfactory, the author sought to obtain a clear solution containing all the chlorine, by dissolving the powder in an alkaline liquid. This is conveniently done by adding, say 10 grams of bleaching powder to 20 grams of sodium carbonate, filtering out the precipitated calcium carbonate, washing the latter until the wash-water no longer discharges the colour of dilute sulphate of indigo, and making up the filtrate to the measure of 1 litre. It is a clear colourless liquid of sp. gr. 1·007. Most satisfactory results

* Gazzetta chemica Italiana, i, 472. † Il Nuovo Cimento [2], iii, 1870.
‡ Chem. News, xxiv, 75.

are obtained from it by all the chlorimetrical methods, and it has the additional advantage of showing, if required, the amount of lime in a sample by adding a solution of sodium carbonate of known strength until a precipitate is no longer formed. This solution is manufactured and used in the north of Ireland for bleaching fine linens; and from the ease and accuracy with which its percentage of chlorine was obtained, the author was led to investigate the feasibility of converting bleaching powder into it for chlorimetrical purposes, and obtained the above results. J. W.

The Estimation of Sulphur by Barium. By E. F. TESCHEMACHER and J. DENHAM SMITH.*

NOTWITHSTANDING that a soluble salt of baryta appears to have been used from the beginning of the art of chemical analysis, as the most trustworthy agent for determining the amount of sulphuric acid present in solutions, the authors feel compelled to state emphatically, after a patient investigation of the process, and by operating upon substances the percentage composition of which could be accurately calculated, that in every instance of such a determination of sulphur, or sulphuric acid, the results are not trustworthy, and, indeed, that they only approximate to accuracy, when the error in the weight of barium sulphate obtained may chance to be compensated by an imperfect purification from adherent salts.

The first point noticed is that barium sulphate is notably soluble in hot and but moderately diluted hydrochloric acid. They have observed that when the precipitated sulphate is washed with hot dilute hydrochloric acid, and the filtrate and washings allowed to remain undisturbed for some time, the sides and bottom of the vessel become covered with a film of barium sulphate, gradually deposited from the previously clear and bright filtrate, a proof that a certain amount of barium salt must have been lost by solution. They admit that the solubility of the sulphate in hydrochloric acid has been already pointed out, but consider that the importance of this fact has been underrated, and esteemed as but little likely to affect the estimation of sulphur by barium.

In a similar manner, they take objection to the inadequate attention which they consider is paid by chemists to the very marked tendency which barium sulphate exhibits, to carry down with it during precipitation variable quantities of other salts contained in solution, such as those of soda, potash, magnesia, baryta, &c., and especially draw attention to the adhesion of barium chloride to the precipitated sulphate, since, although it is well known that it is very difficult to remove all traces of nitric acid, when barium nitrate is employed as

* Chem. News, xxiv, 61—64, and 66—69.

the precipitant, it is generally considered that by careful and assiduous washing, all traces of barium chloride may be effectively got rid of.

Again, they find that barium sulphate is sensibly reduced, when ignited to redness in the usual manner; so that the evidence of the presence of baryta on treating the ignited sulphate with water or dilute acid, must not be regarded as proving that nitrate or chloride has adhered to the precipitate. Thus some precipitated and ignited barium sulphate, when treated first with water, and then with diluted hydrochloric acid, washed, and re-ignited, and again treated with water and dilute acid six times consecutively, yielded each time traces of chlorine and baryta to water only, and a considerable amount of baryta to dilute acid, which is considered sufficient proof that, at all events, a slight reduction had taken place. Moreover, owing to the marked solubility of the sulphate in strongly acid solutions, its purification in the above manner can tend only to widen the error, and to cast still graver doubts upon the trustworthiness of the results obtained.

With the view of ascertaining with what degree of accuracy it was possible to estimate sulphuric acid, it was requisite to obtain a soluble sulphate of stable composition, the basic element of which would not adhere to the barium sulphate, and crystallised ferrous sulphate was selected. With this salt, carefully purified, a series of nine experiments was made, and from 108·6 grains = 91·02 grains of barium sulphate, a mean of 91·694 grains of sulphate was obtained, the highest number being 92·9, and the lowest 90·8 grains; the ignited sulphate was a pure white and soft powder, yielding both chlorine and baryta to water, and still more baryta when treated with dilute nitric acid. Since it has been shown that a certain amount of baryta must be lost by solution, during the process of washing, it is supposed that in eight out of the nine experiments, barium in some form has combined with the precipitated sulphate, and thus brought about an increase in the total weight obtained. In order that the investigation might more closely resemble the actual estimation of sulphur in pyritous minerals, the 108·6 grs. of ferrous sulphate taken as in the previous instance, were peroxidized with nitric acid, the excess of acid removed by careful evaporation, and the sulphuric acid estimated. Instead of 91·02 grs. of sulphate, 89·627 grs. was the mean of the result, the highest number being 91·0, and the lowest 87·05 grs. Here the reverse of the preceding experiments obtains; in no case is there an excess of weight of the precipitate, the loss being more worthy of remark from the discoloration of the precipitate by oxide of iron, the colour varying from buff to a deep salmon tint; and since chlorine and baryta soluble in water and acid were present in all the precipitates, the actual loss of sulphate would seem in every case to be even greater than the apparent loss.

Results similar to the foregoing were obtained when the sulphur of pyrites was estimated. A sample known to contain 49 per cent. of sulphur yielded sometimes a number close upon the truth, sometimes having a variation as great as 2·0 per cent.; and especially did the numbers depart more widely from the truth, when the resulting sulphate was submitted to the process of purification.

The facts pointed out in the foregoing series of experiments have gradually led to a method of estimating sulphur by barium, and more especially the sulphur of pyrites, which experience and continued use have proved to the authors to be exact, trustworthy, and capable of yielding constant results. The method is a volumetric one, based upon the following five conditions, viz. :—

The use of a standard solution of barium chloride *by weight.*

The complete oxidation of the sulphur, and subsequent expulsion of all the nitric acid.

The avoidance of a large excess of hydrochloric acid in the solution.

The avoidance of large quantities of solutions.

The use of considerable weights of pyrites in the analysis.

In preparing the standard solution of barium chloride, it is convenient in practice to make it of such a strength that 1,000 grains by weight shall be equal to and represent 25 grains of sulphur. It should be slightly acidified with hydrochloric acid to prevent the subsequent deposition of barium carbonate.

To prove the accuracy of this standard solution it must be carefully analysed, which is best effected in the following manner. A weighed portion, heated nearly to boiling, is added to a boiling solution of dilute sulphuric acid containing an excess of acid, and the precipitated sulphate is collected and weighed. In this case the barium sulphate obtained yields traces only of chlorine to water after ignition, but if this order be reversed, and the diluted acid added to the solution of barium chloride, so that this latter is in excess during precipitation, then the barium sulphate will be found to yield abundant evidence of barium chloride when treated with water after ignition.

The average exactness of this proceeding is in great measure due to the insolubility of barium sulphate in dilute sulphuric acid; yet it is considered more advisable to rely upon the results afforded by crystallised ferrous sulphate, and to employ a volumetric instead of a gravimetric method.

The authors explain the working of their process by a description of the estimation of sulphur in pyrites. The sample is first carefully selected, powdered, and thoroughly mixed, then in small quantity brought to an impalpable powder by grinding in an agate mortar. 200 grains are taken and dried at 100° C., after which about 30 grains are weighed and placed in a flask of about 20 ozs. capacity. The ore is

then oxidised with 300 grains weight of aqua regia, to which 200 grains of fresh hydrochloric acid are added. When the energetic action ceases the whole is evaporated *just* to dryness, a point which demands care and watchfulness to hit. 100 grains more hydrochloric acid are then added to the flask to redissolve the contents.

A small flask holding some 1,000 grains of standard solution, with dropping tube, is now counterpoised, and so much of the solution transferred to a porcelain basin as practice shows may be looked for as nearly equivalent to the strength of pyrites in sulphur. The contents of the basin are next heated nearly to boiling, and poured into the test solution of the pyrites, then the whole is returned to the basin from the flask, and the latter washed out with a small quantity of water. The liquid is then boiled rapidly, and a small damped filter being in readiness, a little of the mixed solution is filtered, and a portion of the filtrate added to about 3 or 4 grs. of standard barium solution placed from the counterpoised flask in a test-glass. Should a further precipitate be produced, this tested solution is to be returned to the basin with the rest of the filtrate, and so much more solution of barium added as may be judged requisite. This is again boiled and filtered, using the same filter, and tested as before, this operation being repeated until a precipitate ceases to appear with the barium solution, when the weight of the solution employed is taken and noted. It frequently happens that when the operation is complete, both barium and dilute sulphuric acid show a cloudiness in the filtrate after the lapse of a few minutes. When this is the case, the precipitation has been successfully conducted.

It is stated that by the method above described the amount of sulphur in pyrites may be determined with accuracy and certainty to $\frac{1}{10}$th per cent., and that in execution it will be found more simple and expeditious than the old gravimetric method.

Messrs. Glendenning and Edger (Chem. News xxiv, 140) attribute the variations in the results above detailed, to the fact that the precipitated barium sulphate carries down with it a certain quantity of iron sulphate, and adduce experiments tending to show that when this salt is washed out of the precipitate by water and hydrochloric acid, the sulphur in the washings reprecipitated by barium chloride, and the small precipitate of barium sulphate thus obtained added to the original precipitate, concordant results may be obtained.

The following were the results of the analyses of four samples of pyrites:—

25 grains were carefully oxidised and precipitated by barium chloride in the manner generally adopted in analyses of this mineral. The precipitated liquors were allowed to stand in a warm place for eight hours,

then filtered, and the barium sulphate washed with boiling water and hydrochloric acid. The whole of the washings after addition of a little barium chloride were evaporated to dryness, and the quantities of barium sulphate obtained, amounting generally to 0·5 grains, added to the original precipitates, three of which, after ignition and weighing, were treated with about 500 grs. of strong hydrochloric acid, and allowed to stand for twelve hours. The small quantities of sulphate dissolved by the acid were recovered, and added to their respective precipitates.

No.	Before treatment with HCl.		After treatment with HCl.	
	Grs. $BaSO_4$.	Grs. S.	Grs. $BaSO_4$.	Grs. S.
1.....	83·12	11·415	83·08	11·411
2.....	83·18	11·423	83·12	11·415
3.....	83·30	11·410	83·23	11·430
4.....	83·23	11·430		

A reply to these observations has been published by Messrs. Teschemacher and Smith, in the Chemical News for October 13th, p. 171.

J. W.

Estimation of Sulphur in Coal and Coke. By F. C. Calvert.*

The method usually adopted for the estimation of sulphur in coal and coke, consists in adding to an oxidizing *aqua regia* a known weight of the finely powdered material, and after digesting it at a moderate temperature until the whole of the sulphur is supposed to be converted into sulphuric acid, determining the latter by barium in the usual way.

In operating in this manner there are several serious sources of error.

In the first place, the figures obtained include the sulphur or sulphuric acid combined with calcium, as well as that existing as pyrites in the coal; and it is obviously most important in a metallurgical point of view, that these figures should be returned separately, since the sulphur combined with the calcium, as sulphate or sulphide, is perfectly harmless, while the pyrites seriously affects the quality of the iron, by combining with it as ferrous sulphide during the process of smelting.

Again, in carrying out the above-mentioned process, unless the nitric acid be carefully and entirely removed by evaporation, grave errors in the weight of barium sulphate will ensue, and in the present instance it so happens that, if the evaporation of the *aqua regia* be

* Chem. News, xxiv, 76.

carried too far, a basic iron sulphate is sometimes formed, which even long boiling with water fails to remove from the carbonaceous mass, so that a deficiency of sulphur is entailed.

To remedy these defects, the author operates in the following manner:

A weighed portion of the finely powdered coal is boiled in water with an equal weight of sodium carbonate for twenty hours, by which means the calcium sulphate is decomposed, while the iron sulphide remains unattacked. The residue is then filtered, and rapidly washed with boiling water. If a coke has been taken, nitric acid in slight excess must be added to the filtrate, to convert the sodium sulphide into sulphate, and the sulphuric acid determined in the usual manner. The sulphur found in the residue will then correctly represent the amount of pyrites present in the coal.

In estimating this latter, the author objects to the dry oxidizing process, since it invariably entails a slight loss of sulphur. If *aqua regia* be employed after the acid liquor has been concentrated, sodium carbonate must be added in excess, and the whole heated to near the fusing point. By this means the iron, silica, and alumina are rendered insoluble; the mass is then treated with water, washed well, and the filtrate acidified with acetic acid; barium chloride will now precipitate the whole of the sulphuric acid from this solution.

The figures in the subjoined table contrast the results obtained from three distinct samples, when analysed by the old and by the improved method.

	Old process.		New process.		In washings.		Difference.
	Sulphur per cent.	Mean.	Sulphur per cent.	Mean.	Sulphur per cent.	Mean.	
1..	1·36 1·40	1·38	0·60 0·58	0·59	0·79 0·78	0·79	0·79
2..	1·59 1·55	1·57	0·63 0·67	0·65	0·97 0·95	0·96	0·92
3..	1·78 1·73	1·75	0·89 0·85	0·87	0·85 0·88	0·87	0·88

J. W.

Detection of Carbon Bisulphide. By F. SESTINI.*

THE presence of this compound in solution may be detected by its reaction with the hydrates of the alkaline earths (p. 1024). When a mixture of 1 c.c. carbon bisulphide, 5 c.c. milk of lime, and 10 c.c. water, is heated for two hours to 45°—50° in a stoppered flask, and

* Gazzetta chimica Italiana, i, 475.

then left to cool, the liquid first acquires a red colour, and then deposits magnificent prisms of the compound $3CaH_2O_2.CaCS_3 + 7aq$. The same reaction is apparent with only 0·5 c.c. of carbon bisulphide.

On mixing 10 c.c. of a saturated aqueous solution of carbon bisulphide (containing $\frac{1}{1000}$ of CS_2) with caustic potash, heating to 50°, and adding acetate of lead, the liquid yields, after five minutes, a copious black precipitate of lead sulphide. The same reaction is still perceptible with a saturated aqueous solution of the bisulphide diluted with ten times its volume of water, containing, therefore, only $\frac{1}{10000}$ part of CS_2. H. W.

New Precipitating Reagent of Copper. By Hugo Tamm.*

The author proposes to substitute a mixture of equal weights of ammonium sulphocyanate and ammonium acid sulphite for the well known mixture of potassium sulphocyanate and sulphurous acid, as a reagent in the estimation of copper. The copper is precipitated in solutions containing excess of hydrochloric acid, as insoluble cuprous sulphocyanate, which salt, when thoroughly washed and free from hydrochloric acid, which it retains with considerable energy, and dried, has the composition $(Cu_2)''Cy_2S_2$, and contains 52·3 per cent. of copper. It may be converted into the sulphide Cu_2S, by calcination with sulphur in a current of hydrogen, a proceeding especially to be recommended, inasmuch as it is exceedingly difficult to obtain the cuprous sulphocyanate perfectly free from water.

The author has employed this method (which was introduced many years since by Rivot), for the estimation of copper in Swedish copper, bar copper, pyrites, and various alloys, and recommends it as the most exact process for precipitating copper, provided that metal is present in considerable quantity, and more especially when, after the separation of the copper, it is intended to examine the filtrate for foreign metals. J. W.

Determination of Nickel by the Battery. By J. M. Merrick.†

In order to ascertain whether the electro-deposition of nickel was capable of being utilised as a means of estimating this metal, and whether, as in the case of copper, the method was simple in application, the following analyses were undertaken. The method adopted was as follows:—A platinum crucible holding the solution to be decomposed, was made the negative pole of a two- or three-cell Grove's battery, by placing it in the coiled up end of the wire from the zinc plate, and the circuit was completed by dipping into the solution, through a perforated

* Chem. News, xxiv, 91. † Chem. News, xxiv, 100.

porcelain cover, a platinum wire from the other pole. Some pure double sulphate of nickel and ammonium was first analysed. The results are given in percentages.

	I.	II.	III.	Theory.
Metal obtained ..	14·79	14·78	14·77	14·72

The next salt experimented with was commercial nickel sulphate, roughly dried between folds of filter paper.

	I.	II.	III.	IV.	V.	Theory.
Metal obtained..	22·07	21·87	21·84	21·43	22·05	20·71

In this case, the extreme difference is 1·36 per cent., and the least 0·72 per cent.; the salt probably was not quite definite, and no attempt was made to purify it.

The double sulphate of nickel and potassium, twice recrystallised, and presumably pure, was analysed by the aid of the battery, ammonia in excess being added, to prevent the deposition of oxide instead of metal.

	I.	II.	III.	Theory.
Metal obtained ..	13·33	13·37	13·22	13·29

Here the variations of the different analyses were much less than in the previous instance; the results show that the weight of the electro-deposited metal very accurately represents the percentage of nickel in solution. The author further endeavoured to effect the separation of nickel from copper, and from some other metals, by the same agency, and was partially successful, but reserves the details for a future communication.

J. W.

Recovery of Molybdic Acid from Residues. By R. Fresenius.*

The process recommended by the author consists in evaporating the residuary solutions to dryness, and igniting till the ammonium nitrate has for the most part been destroyed; the residue is then digested with ammonia, which dissolves out the molybdic acid. The filtered solution is treated with sufficient magnesia mixture to precipitate any phosphoric acid that may be present. The precipitate, if any, is allowed to subside well before filtering, and to the filtrate is added just sufficient nitric acid to render the liquid slightly acid. Molybdic acid is thus precipitated, and may be obtained pure by syphoning off the supernatant liquid, and washing with a little water. The filtrate contains but little molybdic acid, and can be worked up

* Fres. Zeitschr. für anal. Chem., x, 204.

again with fresh residues. Fresenius gives the preference to this method over that of Muck,* which depends upon the precipitation of the molybdic acid by means of sodium phosphate (1 part of phosphoric acid to 30 of molybdic acid). The yellow precipitate is thrown on a filter and washed with water, till the filtrate appears milky, then dried at 100° C., and the phosphoric acid separated by the addition of 2 to 3 parts of magnesia (nitrate), to a solution of the precipitate in the least quantity possible of ammonia. The magnesium precipitate is washed with the remaining quantity of ammonia (altogether 350 parts for every 100 parts of yellow precipitate), and the ammoniacal filtrate added to the nitric acid (1,350 parts by weight for every 100 parts). After long standing, a small quantity of a yellow precipitate usually separates, which should be filtered off. The filtrate, which contains about 5 p. c. of molybdic acid, is now again ready for use.

W. V.

New Test for Alcohol. By M. Berthelot.†

In those cases in which it is desired to determine with certainty the existence of alcohol in presence of a large quantity of water, the following method is recommended:—Chloride of benzoyl is decomposed very slowly by cold or lukewarm water; but, if the water contains alcohol, benzoic ether is immediately formed; the ether is found with the excess of chloride of benzoyl. The presence of the ether can be made manifest by heating a drop of the chloride of benzoyl with aqueous solution of potash, which dissolves the acid chloride almost immediately, without acting at first on the ether. The reaction is very distinct in working with 20 to 25 c.c. of water containing a hundredth part of alcohol. Even with a thousandth part of alcohol, when some cubic centimetres of liquid are used, the smell of the benzoic ether is very apparent.

W. H. D.

Determination of Glacial Acetic Acid. By Fr. Rüdorff.‡

The volumetric estimation of acetic acid by means of a standard solution of caustic soda cannot claim very great accuracy, because the change in colour of litmus is not sufficiently marked. Rüdorff has therefore proposed a new method, readily executed and very accurate, which consists in determining the solidifying point of the acid.

Commercial glacial acetic acid is never free from water, the solidifying point of various samples ranging from 7° to + 14°. In order

* Zeitschr. für anal. Chem., viii, 377. † Comptes rendus, lxxiii, 496.

‡ Wittstein's Vierteljahrschr. f. prakt., Pharm., 1871, p. 84; Pharm. J. Trans. [2], ii, 241.

to obtain the acid perfectly anhydrous, a quantity of the commercial glacial acid was left in a cold place, until about three-fourths of it had solidified; the liquid part was separated, and this operation was repeated till a constant solidifying-point was obtained.

The glacial acid thus prepared solidifies at 16·7°, and boils at 117·8°. By gradual cooling the temperature may be reduced to 10°, and even 8·5°, and the acid may be shaken without solidifying; but a single grain of solid acid sets the whole mass at once, the temperature rising to 16·7°. When it is melted by placing the vessel in water of about 25°, the thermometer placed inside the acid indicates 16·7°, as long as a considerable quantity of solid substance remains, proving that the melting and solidifying points are at the same temperature.

100 parts by weight of anhydrous acid were mixed with a weighed quantity of water, and the solidifying-point of the mixture was determined. The proportion of acid and water would be altered if much acid solidified; it is therefore necessary to take care that only very little acid separates. This is effected by cooling the mixture to within one degree of the solidifying-point, approximately determined; after which a particle of solid acid is added, and the liquid well stirred with a delicate thermometer. Repeated experiments showed a difference of not more than 0·1°. The following table contains the results of a series of observations, viz.:—

100 parts by weight of acid mixed with water.	100 parts of mixture containing water.	Solidifying-point. Degrees.
0·0 Water.	0·0 Water	+16·7 C.
0·5	0·497	16·65
1·0	0·990	14·80
1·5	1·477	14·00
2·0	1·961	13·25
3·0	2·912	11·95
4·0	3·846	10·50
5·0	4·761	9·40
6·0	5·660	8·20
7·0	6·542	7·10
8·0	7·407	6·25
9·0	8·257	5·30
10·0	9·090	4·30
11·0	2·910	3·60
12·0	10·774	2·70
15·0	13·043	− 0·20
18·0	15·324	2·60
21·0	17·355	5·10
24·0	19·354	7·40

The table shows that, especially in concentrated acid, one tenth of a percentage of water may be accurately determined.

Several other substances act like water in reducing the solidifying-point of acetic acid; for instance, sulphuric acid, alcohol, and several salts soluble in the acid. A mixture of 100 parts of acetic acid and 0·5 part of sulphuric acid solidifies at 16·4°; 100 parts of acid and 1·8 part of alcohol at 15·25°. The influence of water may be partly counteracted by sulphuric acid; thus, from a mixture of 100 parts of acid and 10 parts of water the acid separates at 4·3°; an addition of 2 parts of sulphuric acid raises the point to 5·8°, and 20 parts of sulphuric acid added to the same mixture bring the point up to 10·7°.

The solidification of acetic acid takes place completely, even in summer. The acid is cooled to about 10° or 12°, a particle of solid acid is added, and on shaking the bottle the acid solidifies forthwith. A small quantity of solid acid is easily obtained by placing a test-tube containing a few drops of liquid acid in a mixture of chloride or nitrate of ammonium and cold water.

Determination of Sugar and Detection of Albumin in Urine.
By Prof. Seegen.*

The author having tested all existing methods for this determination, concludes that we have no reagent capable of detecting the presence of minute traces of sugar dissolved in urine with certainty, and to the exclusion of other analogous substances. Normal urine does not contain it in sufficiently large quantities to allow of its determination. Normal urine contains minute quantities of reducing substances, but whether they consist of sugar, partially or wholly, cannot be determined with our known tests.

To detect albumin, the precipitate obtained by heating urine with nitric acid is carefully washed to remove the last traces of urine, then redissolved in a little potash, and a few drops of Fehling's copper solution are added. A fine violet coloration is instantly produced, especially with a strong solution; the reaction is very characteristic, and readily shows one per cent. of albumin.

Use of Polarized Light for the Estimation of the Value of Cinchona-barks.
By O. Hesse.†

This communication consists essentially of a review of a paper by De Vry‡ on the same subject. The latter believes that, by estimating the rotating power of a solution of the total alkaloïds contained in a bark,

* Pharm. J. Trans. [2], ii, 202. † Deut. Chem. Ges. Ber., iv, 692.
‡ Page 857 of this volume.

and also of a solution of the alkaloïds insoluble in ether, the value of the bark can be obtained. Hesse points out that of the alkaloïds contained in cinchona barks, the rotating powers of only two, viz., quinine and quinidine, are known with accuracy. Moreover, the Java barks contain, according to De Vry and Jobst, an amorphous base, and Hesse has found in some Neilgherry barks, paricine, and two substances the relative rotating powers of which are almost unknown. It may, however, be possible to determine the amount of quinine present by precipitating the neutralized sulphuric acid solution of the mixed alkaloïds with sodio-potassic tartrate, dissolving the precipitated quinine and quinidine tartrates in dilute sulphuric acid, and estimating its power of rotation. Between these alkaloïds there is considerable difference in rotating power, which also would extend to their tartrates, thus for quinine in alcoholic solution $\alpha_j = -184{\cdot}35°$, and for quinidine in alcoholic solution $\alpha_j = -113°$.

Thus it will be seen that the method proposed originally by De Vry can, at the best, give only approximate results.

A. P.

Spectroscopic Characters of the Ammoniacal Solutions of Carmine, Cochineal, and other Substances. By G. Campani.*

An ammoniacal solution of carmine, examined by the spectroscope, exhibits two dark absorption-bands between the Fraunhofer lines D and E, like those of blood, one situated at 8°, the other at 9°—10° of a spectroscope having a scale of 20°, in which the sodium line falls at 7·7°. With such a spectroscope, therefore, it would be impossible to distinguish an ammoniacal solution of carmine from that of blood.

The aqueous solution of cochineal does not exhibit any dark bands, but on adding ammonia in quantity sufficient to give the solution a red colour inclining to violet, the two dark bands of the ammoniacal carmine solution make their appearance.

A solution of murexid gives a dark band at 7·5° to 10°; the addition of potash in quantity sufficient to change the colour to violet does not alter the spectroscopic appearance.

A decoction of madder is inactive in the spectroscope, even after addition of ammonia.

H. W.

Technical Chemistry.

On the Existence of Copper in Certain Waters. By M. Roux.†

Suspicion having arisen that an epidemic which had broken out in a village was due to the water of a fountain being contaminated with

* Gazzetta chemica Italiana, i, 471. † J. Pharm. [4] xiv, 104—110.

the refuse of an adjacent copper factory, the author was requested to examine into the matter. He found, however, that this water contained only traces of copper, and that the water of a well situated at 90 metres from the factory was quite free from copper, whereas that of a well situated at 150 metres from the same factory contained a large amount of that metal. Further examination showed that the presence of the copper in this water was due to the use of copper pumps and pipes, copper, as is well known, being acted upon by water containing air and carbonic acid, or by salts, such as alkaline chlorides. To prevent such contamination, the author suggests the use of pumps of bituminous iron, or of copper or iron plated with tin.

Examination and Composition of Cements. By C. BENDER.*

ROMAN and Portland cements are compounds of alumina, lime, and silica in closer or looser combination according to the temperature at which they have been burnt. Besides the constituents above named, magnesia, potash, soda, and generally sulphuric and phosphoric acids are also present. Of these subsidiary bodies, sulphuric acid (as gypsum) is so hurtful to the quality of the cement, that if a sample contains any considerable quantity—even 3 per cent.—it should be rejected. The gypsum is burnt dead at the temperature employed in making the cement, and does not combine with water until after the rest of the mass has hardened, and then, as it slowly takes up water and expands, it causes the whole to crumble. Much magnesia seems also to injure the quality, but a moderate proportion of soda improves it. C. H. G.

Extraction of Animal Fats to be used for Food, or for the Preparation of Cosmetics. By H. POHL.†

THE fresh raw fat, freed as far as possible from fleshy matters, is cut into thin slices and washed free from blood, &c., with the purest cold water that is obtainable. The washed fat is then placed in a cylindrical stoneware vessel, 1·25 metre high and ·5 metre wide, standing in a water-bath which can be heated by steam. A cock of wood or stoneware at the bottom of this vessel enables it to be emptied without removal from the water-bath. After the cylinder has been three-fourths filled, a kind of sieve of stoneware is laid on the surface of the fat; 10 per cent. of *pure* highly diluted hydrochloric acid is added, and a well fitting cover of stoneware is laid over the top. The dilute acid used is prepared by adding 3 lbs. pure hydrochloric acid (sp. gr. 1·12

* Chem. Centr., 1871, 510. † Dingl. polyt. J., cci 254—257.

to 100 lbs. water). On warming, as the fat melts in the cells, the acid dissolves the membranous portions, and the sieve gradually sinks to the lower part of the cylinder, carrying with it the skinny matters and unmelted fat, while the pure melted portion collects in the upper part of the vessel. When all the fat is melted, the dilute acid solution is run off at the bottom, and the fat is washed two or three times with boiling water, to the last portion of which a little carbonate of magnesia is added to ensure perfect neutralisation.

The washed fat is dissolved in an equal volume of Canadian oil, which separates a nitrogenous matter. The solvent is then recovered by distillation. The resulting fat is scentless and tasteless, almost colourless, and is absolutely neutral. It contains no trace of water or of nitrogenous matter, and therefore remains free from all tendency to become rancid when kept. C. H. G.

On the Preparation of an Oxidised Aniline-black. By ARMAND MÜLLER.*

THE paste is thus prepared:—20 grms. chlorate of potash, 40 grms. sulphate of copper, 16 grms. chloride of ammonium, and 40 grms. hydrochlorate of aniline are dissolved in 500 c.c. water warmed to about 60°, and removed from the water-bath. In about three minutes the solution froths up and gives off vapours which strongly attack the breathing organs. If the mass is not quite black after the lapse of a few hours, it is again heated to 60°, and then exposed in an open place for a day or two, and afterwards carefully washed out till no salts are to be found in the filtrate. For use in printing, the black paste is mixed with a somewhat large quantity of albumin, and the goods after printing are strongly steamed. The paste can be pressed into moulds and used as a substitute for Indian ink. When thoroughly dried *in vacuo* it appears as a black powder, which contains C = 39·28 per cent., H = 7·41 per cent., N = 7·41 per cent., corresponding to the formula $C_{24}H_{14}N_2O_{22}$, which requires C = 39·87 per cent., H = 3·86, N = 7·72. This formula is given under reserve. C. H. G.

Iodine-green on Alpaca, with Water-glass. By FERD. SPRINGMÜHL.†

THE damped stuff is worked in a bath of about $\frac{1}{4}$ lb. iodine-green (in powder), $\frac{1}{4}$ lb. spirit of ammonia, some sulphuric acid, and $\frac{1}{4}$ lb. soda water-glass for each 10 lbs. stuff for a short time, drawn through a hot tannin solution, returned to the first bath, and lastly brightened in a somewhat strong acetic acid bath. C. H. G.

* Dingl. polyt. J., cci, 363. † Dingl, polyt. J., cci, 374.

*Notice of a new Photo-lithographic Process.**

An ordinary carbon picture developed on lithographic stone, instead of on glass or zinc, can be inked and printed from in the ordinary manner. The development of such a picture can be obtained by the following process:—

Carbon paper is floated for two minutes on a bath of pure red chromate 1 part, water 10 parts; dried in an air-tight box over fused chloride of calcium; exposed under a sharp negative for $\frac{3}{4}$ to 1 minute to sunlight, or for 4 to 10 minutes to diffused light; dipped in cold water; and laid face downwards on a well polished lithographic stone. A sheet of blotting-paper is laid on the back and rubbed with a rubber pad all over; the blotting-paper is renewed; and the rubbing is continued till the paper is half dry. After three or four minutes the stone is laid slanting in a dish and overflowed with hot water; the black gelatin swells up and the paper softens; the washing with hot water is continued till all the paper can be pulled away without resistance. On the stone there is left a formless mass of black gelatin, which gradually develops into a clear picture on continuing the washing with hot water. When the picture is quite clear, the stone is laid in cold water, and when cold is propped against the wall and allowed to dry in the air. The dry picture is treated with a solution of gum, &c., in the usual way. C. H. G.

Cheap Preparation of pure Dextrin. By O. Ficinus.—(Dingl. polyt. J., cci, 375.)

On the Examination of Essential Oils. By. H. R. Schramm.†

Copaiba oil can be detected in oil of Neroli by mixing a few drops with spirit and burning the mixture on cotton wool. When the spirit has burnt off, the smell of the copaiba oil can be distinguished.

Use of Tannin for the Preservation of Wine.—(Dingl. polyt. J., cci, 376.)

On the Manufacture of Dinas-stone (Quartz Bricks). By Carl Bischof.—(Dingl. polyt. J., cci, 339.) An abstract from Percy's metallurgy.

* Dingl. polyt. J., cci, 374. † Dingl. polyt. J., cci, 375.

On the Recovery of Nitrous Acid in the Manufacture of Sulphuric Acid. By Dr. GEORGE LUNGE.*

A DETAILED description, with drawings, of "Glover's towers," as used on the Tyne. Cuts would be required to make an abstract comprehensible.

C. H. G.

New Diffusion Apparatus for extracting the Juice of any Plant, especially of the Sugar-beet and Sugar-cane. By JULIUS ROBERT.—(Dingl. polyt. J., cci, 257—262.) Requires a plate to render the description intelligible.

On Schultz's Cold Diffusion Process. By W. FREYN.—(Dingl. polyt. J., cci, 262—266, from the "Marktbericht," June, 1871.)

Treatment of Fruit Juices. By N. GRAGER.—(Dingl. polyt. J., cci, 266—270.)

Improvements in Light-Printing. (Dingl. polyt. J., cci, 276.)—An abstract of a paper by Mr. Edwards in the British Journal of Photography.

Glue Rollers for Light-Printing.—(Ibid., 277.)

On the Apparatus of Giret and Vinas for Heating Wines, with a view to their Preservation. By H. MANGON (ibid. 550—556).

Elkinston's Improvement in the Manufacture of Copper (ibid. 560).

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* Dingl. polyt. J., cci, 341—353.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXVI.—*On the Distillation of Wood.*

By Watson Smith, F.C.S.

I have been much interested in reading Mr. E. T. Chapman's valuable paper on the production of wood-spirit, lately read before the Chemical Society, and I now beg to present the results of certain observations and experiments of my own on the subject.

As regards the kind of wood preferred for distilling, oak is certainly that most generally sought after, oak crop-wood and old oak-timber being the forms most easily obtainable.

The retorts used in the writer's experience were 6 feet long and 3 feet in diameter; others used were 7 feet long and $3\frac{1}{2}$ feet diameter. These retorts (viz., those first mentioned) were charged early in the morning, and finished late at night, the whole operation, after the doors were made up, lasting about 11 hours. The retorts were very hot when the wood was put in each morning. The condensed liquid products of the distillation began to drop $1\frac{1}{2}$ hours after the retort doors were luted up.

The termination of the process was ascertained by handling the exit-pipe from any of the retorts into the main; when this was found to have cooled down, the distillation had ceased. The retorts were allowed to stand till the following morning before they were opened, to withdraw the charcoal. The next morning the doors were opened one by one, and the charcoal was as rapidly as possible raked out into a capacious iron barrow, which, when full, was wheeled to the trap-door or man-hole of an underground vault. The barrow was upset with its load of partially ignited charcoal over the open trap-door, and the charcoal was rapidly shovelled into the vault. The next retort door was then opened, and the charcoal drawn from that, and so on, till all were emptied into the vault. A bucket or two of water was now thrown in, and the trap-door luted down securely.

The mixture of tar and crude wood-acid which came over from the condensers was pumped into a large cistern sufficiently elevated from the ground; there it was allowed to settle, the tar of course forming the lower, and the wood-acid the upper layer of fluid.

When wanted, the tar was drawn off by a tap at the bottom of the cistern, and the wood-acid either by a siphon or by a tap-arrangement.

The gaseous bodies escaping during the process, are carried round by a pipe having a downward dip to the fire-place. Just before turning to the fire-place, the pipe dips into a closed vessel in which any condensed matter may deposit.

The time of greatest luminosity of the gas-flame is invariably just before finishing, though, if the condensation be good, this luminosity is but feeble. The condensation should be such, that no patch of condensed fluid is formed on the hand when the palm is held before the jet of escaping gas—this jet will then be found to be perfectly cold.

Now as to the quantities of tar, crude wood-acid, and charcoal obtained: According to my experience, the following is the average yield which has been obtained, when old oak-timber has been used in the retorts, after being split up and sawn into pieces about, on the average, 2 feet to 2½ feet long, and 3 or 4 inches thick.

	Charcoal.	Wood-acid.	Tar.
1,000 parts by weight of wood yielded..	327	509	55

The wood-acid had a specific gravity of from 1·025 to 1·027.

In order to carbonise one ton of wood, 10½ cwts. of coal were used on the average.

In Muspratt's Dictionary (article Acetic Acid) data are given from which the following results are calculated:—

By Three Works in the neighbourhood of Paris.

	Charcoal.	Wood-acid.	Tar.
1,000 parts of wood yielded	253½	568	82½
Specific gravity of wood-acid = 1·025.			
1,000 parts of sawdust in specially constructed furnace yielded	—	528	50
		Wood-acid and tar.	
1,000 parts of wood yielded	268	577	
Specific gravity of wood-acid = 1·030.			
1,000 parts of oak, in ordinary cylinders	268	—	—

By Mr. Randall, Stroud:—

		Wood-acid and tar.
1,000 parts wood yielded	200	476
Average yield, according to Muspratt's numbers.....	268	577

Specific gravity of wood-acid = 1·030 = 6° Twaddell.

Average yield, according to writer's observations	327	509

Specific gravity of wood-acid = 1·0275 = $5\frac{1}{2}$° T.

Wood used, old oak timber mainly, with some crop-wood, splinters, &c.

I have calculated the yields of various kinds of wood from numbers furnished by Muspratt's Dictionary, in which I may add a most valuable condensed practical account is given of the process (Articles Acetic Acid, Wood-vinegar).

Per 1,000 parts of each Variety.

	Wood-acid.	Specific gravity.	Charcoal.
Beech	536	1·029	250
Birch (cut 3 years)....	357	1·031	208
Oak	566	1·022	271
Maple	431	1·018	229

Oak is certainly the variety of wood most sought after by wood distillers; birch and beech follow next in order of superiority.

It will be noticed that in the average yield, according to the writer's observations, the percentage of charcoal is comparatively large, and that of wood-acid comparatively small. The charcoal in three cases I believe was never thoroughly burnt, and in order to thoroughly carbonise it, the fires ought to have been kept up three or four hours longer. I feel certain that the time allowed for carbonising was too short; in other words, the distillation was conducted too rapidly, and not enough time was allowed for completing the decomposition of the woody fibre. It is quite true, as Mr. Chapman remarks in his paper, that "rapidly charred wood yields a smaller amount of distillate, than when it is slowly charred."

The increased yield, by allowing more time over which to extend the process, would then be due:—

1stly. To the distillation being more slowly conducted, *i.e.*, at a lower temperature.

2ndly. To the carbonisation being more perfect.

According to Muspratt, the amount of coal necessary to carbonise one ton of wood is 7 cwts., *i.e.*, 350 parts per 1,000 of wood.

According to the writer's observations, however, $10\frac{1}{4}$ cwts. or $512\frac{1}{2}$ parts per 1,000 of wood were required. In the latter case, the gas from the escape pipes was not burnt under the fire places; whether it was in the former case, Muspratt does not say, but the difference due to this would be but very small, and would by no means account for such a difference in coal consumed. My opinion is that Mus-

pratt's figure for coal is either too low, or only one which could be secured by the greatest economy, and the most efficient flue and draught arrangements, so that the heat could be utilised to the utmost.

Acetic Acid contained in the Wood-acid received from Condenser.—The following experiments made to determine the amounts of acetic acid contained in the crude wood-acid distilling over at various times during the process, revealed the curious circumstance that the amount of acetic acid thus coming over, gradually increases, but more rapidly (in proportion) than the rate of increase of the specific gravity of the wood-acid up to 1·017; the specific gravity then further increases up to 1·030, at which it remains, the amount of acid beginning to decrease till the finishing of the operation.

The following numbers are the means of three experiments:—Retorts charged at 8 A.M. Distillate commenced dropping at 9.15 A.M.:—

Remarks.	Times of observation.	Grains per gallon of $C_2H_4O_2$.	Specific gravity of wood-acid.
	A.M. 10.15	966	..
	11.30	1575	1·010
	P.M. 1.15	3003	1·015
This sample possessed the spirituous odour of wood-naphtha more strongly than any sample taken	4.15	4200	1·017
The maximum amount of tar came over at this period of any yet attained	5.15	3780	1·030
The amount of tar after 5.15 increases steadily.....	7	3150	1·030
	8	3066	1·030
	10	2940	..
	10.50	2520	..

According to my experience from—

1,000 parts of wood, 20 parts by weight of acetic acid ($C_2H_4O_2$) have been obtained in the form of crude wood-acid.

From data given by Muspratt, the following numbers are calculated:—

Birchwood.....	1,000 parts by weight	yield	22	parts	$C_2H_4O_2$
Young oak	1,000 ,,	,,	36	,,	,,
Hawthorn.....	1,000 ,,	,,	44	,,	,,
Willow	1,000 ,,	,,	9	,,	,,

The next point to be observed is the amount of wood-spirit yielded by a given weight of wood.

I have noticed the following results as obtained on two different occasions:—

1. 20 cwts. of wood yielded 1·7 gallons of wood-spirit at 862 sp. gr.
   or 1,000 parts would yield 85 ,, ,, 862 sp. gr.
2. 318 cwts. of wood yielded 18 ,, ,, 885 sp. gr.
   or 1,000 parts would yield $56\frac{1}{2}$,, ,, 883 sp. gr.

Muspratt states that 20 cwts. of wood should yield $1\frac{1}{4}$ to $2\frac{1}{2}$ gallons of spirit, *i.e.*, 1,000 parts should yield from $62\frac{1}{2}$ to 125 gallons of spirit. Mean 93·7 gallons.

Now not only the aqueous acid distillate from the retorts, but also the deposit of tar which settles down to the bottom of the wells in which the products of condensation accumulate, contains a considerable proportion of wood-spirit. Of this fact I believe many manufacturers are ignorant. In both the examples I have given above the wood-tar was *not* distilled for the sake of the naphtha it contained: hence, if it had, the returns would have no doubt been higher.

On the average, from every 100 gallons of wood-tar it is possible to obtain by distillation 3 gallons rectified wood-spirit.

The following fractional distillations were made, with a view to ascertain the best mode of separating the naphtha or wood-spirit from the various other bodies contained in the wood-tar, by repeated rectification:—

No. 1 Sample of Tar.		No. 2 Sample.	
Temp. centigr.	Per cent. by volume distilling over.	Temp. centigr.	Per cent.
		At 85°	14
At 90°	13	Below 100°	$16\frac{1}{2}$
Below 95°	10	,, 110°	5
,, 120°	$2\frac{3}{4}$	From 110° to 150° only a few drops came over.	
,, 180°	$14\frac{1}{4}$		
,, 195°	10	Below 160°	5
,, 210°	7	,, 180°	5
		,, 200°	6
Total	57	$51\frac{1}{2}$ p.c. distills over below 200° C.	

No. 3 Sample.		No. 4 Sample.	
From 85°—95°	$10\frac{1}{2}$	Below 100°	22
,, 95°—100°	32	,, 200°	$9\frac{1}{2}$
		,, 230°	$8\frac{1}{2}$
Total	$42\frac{1}{2}$	Total	40

35,000 grain measures of wood-tar were distilled in a small iron still, over a Bunsen's lamp :—

Temp. centr.	Grain measure distilling over.	On standing, each distillate separates as follows :—	Per cent. by vol.	Remarks.
Cent.	Gr.meas.	Gr. meas.		
72° to 100° ..	3020	Into 2,100 watery liquid " 920 oily body insoluble in aqueous fluid.....	$8\frac{1}{2}$ (*a*)	Began to distil over at 72° C.
Below 110° ..	1700	" 1,300 aqueous fluid " 400 oily "	$4\frac{3}{4}$ (*b*)	Distilled over most vigorously, and in largest quantity, at 92° C.
" 150° ..	1150	" 925 aqueous " " 225 oily "	$3\frac{1}{4}$ (*c*)	
" 205° ..	1850	.. .. ..	$5\frac{1}{2}$ (*d*)	
		Total.....	22	

The watery portions separating in those fractions marked (*a*), (*b*), and (*c*), were of a dirty orange colour, and possessed a very pungent odour, also attacking the eyes and mucous membrane of the nose.

The oily portions were separated from the aqueous by means of a tap-funnel.

(*a*). The oil separating from the aqueous fluid (marked *a*) distilled at the following temperatures :—

Temp. cent.	Per cent. by volume.
From 60° to 76°	17·9
Below 86°	9·7
" 96°	5·9
" 110°	6·0
" 120°	5·9
" 130°	6·0
" 140°	5·9
" 155°	7·6
	64·9

The portion remaining behind in the flask smelt very like creosote.

Watery portion separating from the fraction marked *a* :—

Temp. cent.	Per cent. by volume.
Below 70°	3
,, 80°	2
,, 85°	$2\frac{1}{2}$
,, 90°	$7\frac{1}{2}$
,, 99°	17
	32

The remainder left in the flask refused to ignite on application of a flame.

(*b*). Aqueous portion separating from fraction *b*:—

Temp. cent.	Per cent. by volume.
Below 70°	0
,, 80°	0
,, 85°	0
,, 90	0
,, 99	12

(*c*). Aqueous portion separating from fraction *c*:—

Temp. cent.	Per cent. by volume.	
90 to 100	28	Weak spirit, almost clear and colourless.
	5·8	Orange-coloured oil.
Total	33·8	

From these distillations I conclude, that in thus distilling the wood-tar, that which comes over is a mixture of wood-spirit much diluted with water, with creosote and other bodies of high boiling point. These higher-boiling, oily bodies separate from the aqueous portion of the distillate, retaining a quantity of wood-naphtha dissolved in them. The aqueous portion from which these oils separate also contains spirit in solution. By rectification this wood-spirit can be obtained from both oils and from the weak aqueous solutions, as the above experiments testify.

Wood-spirit and Lime Acetate.—To obtain the wood-spirit from the crude wood-acid, the latter may be distilled alone by steam-heat or fire directly applied, and in either a copper or iron still. (Of course the use of an iron still will depend on whether the manufacturer cares for the presence of iron in his pyroligneous acid or not. When he uses it to make iron liquor-mordant, for instance, he does not, of course, fear the presence of iron.)

The distillation is continued till a portion of the distillate no longer

inflames when thrown on the fire. By another method, the manufacturer first saturates his crude wood-acid with lime hydrate, and afterwards distils this crude acetate liquor in a wrought-iron still. By this plan many believe that the naphtha is more easily obtained in a more concentrated form and with less loss than by the other. The crude acetate liquors remaining are evaporated down in pans to dryness, and furnish the *black acetate of lime*. This black acetate is used for making acetic acid. In the first-named process (viz., that in which the wood-acid is distilled alone), the pyroligneous acid remaining, if required for acetic acid making, is first left to stand, so that tarry matter, sediment, &c., may settle from it; it is then run into a tank and there saturated with milk of lime, and allowed to stand again. When sufficiently settled, the clear liquor is pumped or siphoned into an evaporating pan, and boiled down. The liquor is stirred up now and again, and scum, tarry matter, &c., is skimmed off. At length a pellicle of lime acetate forms on the surface; this is skimmed off with a ladle made for the purpose. This skimming off the pellicle of acetate is constantly carried on, the salt being thrown on a drainer or into skips, so placed that the liquors may may run back into the pan. The acetate obtained by this process is known as the "*grey acetate*," and is, of course, considerably purer than the "*black variety*."

The weak wood-spirit obtained in the first distillation, as before mentioned, is further purified and concentrated by one or two rectifications with lime in a copper still. These stills are heated by coils of steam pipe circulating inside them. Two rectifications are generally sufficient. The spirit thus obtained varies from 850 to 880 specific gravity.

1,770 gallons crude wood acid yielded 247 gallons weak spirit after the first distillation. This first distillation was made in a copper still heated with fire.

These 247 gallons were rectified with lime by steam-heat, and 30 gallons of stronger spirit were thus obtained; on rectifying again with lime, 18 gallons of rectified wood-spirit at 880 sp. gr. were obtained.

This was, no doubt, a poor yield, and its being so I believe to be due to the fact that too small a quantity of weak naphtha was distilled off in the first distillation. About a fifth of the wood-acid should be taken off to ensure that all the spirit is extracted.

The last portions distilling over from the rectifying still are of a lemon-yellow colour, and usually have a specific gravity 880.

When this lemon-coloured fluid is shaken with caustic soda-solution, a fine orange-yellow coloured magma is obtained.

These yellow-coloured last runnings have a very pungent odour, and violently attack the eyes and mucous membrane of the nose.

XXVII.—*On Anthraflavic Acid.*

By W. H. Perkin, F.R.S.

In a paper on Artificially Prepared Alizarin, which I had the honour of bringing before the Society some time since,* I mentioned that Dr. Schunck had succeeded in isolating a beautiful yellow crystalline acid which usually accompanies this colouring matter as a secondary product. Dr. Schunck has since published an account of this substance,† which he has named anthraflavic acid, assigning to it the formula $C_{15}H_{10}O_4$.

C. Liebermann, in a paper "On a By-product in the Manufacture of Alizarin," has likewise given an account of a yellow crystalline acid, which, from the description given, appears to be the same body as that examined by Dr. Schunck; he has, however, assigned to it the formula

$$C_{14}H_8O_3, \text{ or } C_{14}H\left\{\begin{matrix} O_2 \\ HO \end{matrix}\right.$$

and regards it as *monoxyanthraquinone*.‡

Seeing that anthraflavic acid accompanies alizarin prepared from pure anthraquinone, it was difficult to understand how it could contain fifteen atoms of carbon, a difficulty observed by Dr. Schunck himself.

Liebermann's formula therefore appeared more probable, inasmuch as it represented this product as an anthracene derivative containing fourteen atoms of carbon. But, seeing the wide difference between these formulæ, and being desirous of knowing the true nature of this acid—both for practical and theoretical reasons—I submitted it to a fresh examination.

The anthraflavic acid examined was prepared from the pure barium salt by means of hydrochloric acid, and, after being well washed and dried, was further purified by two crystallisations from boiling alcohol; from this solvent it was deposited in beautiful bright yellow silky needles, generally arranged from a common centre. Dissolved in concentrated sulphuric acid, it gave, when viewed with the spectroscope, the absorption-band near the edge of the blue, as observed by its discoverer, Dr. Schunck.

The crystallised acid was perfectly anhydrous after drying *in vacuo*, and did not lose weight even when heated to 180° C.

* Chem. Soc. J., xxiii, 143.

† Proc. Lit. and Phil. Soc. Manchester, x, 133.

‡ Deut. Chem. Ges. Ber., iv, 103.

When submitted to combustion, it gave the following results :—

I. ·2302 of substance gave
·5903 of CO_2, and
·0699 of H_2O.
II. ·2400 of substance gave
·6142 of CO_2, and
·0753 of H_2O.

These numbers give percentages agreeing with the formula $C_{14}H_8O_4$, as the following comparisons will show.

	Theory.		Experiment.	
			I.	II.
C_{14}	168	70·00	69·94	69·79
H_8	8	3·33	3·37	3·48
O_4.....	64	26·67	—	—
	240	100·00		

Baric Anthraflavate.—To prepare this salt, it is first necessary to separate anthraflavic acid from commercial alizarin. This may be effected by boiling with baryta-water, filtering off the orange-coloured solution, and precipitating the acid by means of hydrochloric acid ; or by dissolving the colouring matter in a boiling dilute solution of caustic soda and adding milk of lime, until the solution, which is kept boiling, becomes yellow or orange. This is then filtered off from the purple calcium salts, and the acid precipitated with hydrochloric acid.

The crude anthraflavic acid thus obtained is washed on a filter and dried. It is then powdered, boiled with alcohol, and, when cold, the dark-coloured fluid is filtered off. The undissolved product is next treated with dilute caustic soda, and the resulting solution filtered to remove insoluble impurities.* It is then boiled and, after barium chloride has been added in excess, rapidly filtered. On cooling, the baric anthraflavate is deposited in reddish-brown needles, which require three or four recrystallisations from water to render them perfectly pure. The latter part of this process is very nearly the same as that described by Dr. Schunck.

The colour of the cold aqueous solution of pure baric anthraflavate is much like that of potassic dichromate, though rather darker. The crystallised salt ceases to lose weight after being dried at 150°, even if the temperature be raised to 180°.

The following determinations of carbon, hydrogen, and barium were made on specimens dried at 150° :—

* These impurities are present in considerable quantities, and when heated, give a sublimate of pale yellow needles, like anthraquinone, leaving a carbonaceous residue.

I. ·3338 of substance burnt with plumbic chromate gave
·5340 of CO_2, and
·0589 of H_2O.
II. ·3507 of substance gave
·2132 of $BaSO_4$.
III. ·1260 of substance gave
·0768 of $BaSO_4$.

The numbers give percentages agreeing with the formula

$$C_{28}H_{14}Ba_2O_9 = 2C_{14}H_6BaO_4 . H_2O.$$

as the following comparisons will show.

	Theory.		Experiment.		
			I.	II.	III.
C_{28}	336	43·75	43·63	—	—
H_{14}	14	1·82	1·96	—	—
Ba_2	274	35·68	—	35·76	35·83
O_9	144	18·75	—	—	—
	768	100·00			

Dried *in vacuo*, or at 100°, it contains a larger quantity of water, and has the formula

$$2C_{14}H_6BaO_4 . 3H_2O,$$

as the following numbers will show:—

I. ·111 of substance dried at 100° gave
·0646 $BaSO_4$ = 34·22 p. c. Ba.
II. ·2564 of substance dried at 100° lost at 150°.
·0121 of H_2O = 4·7 p. c.
III. ·2568 of substance dried at 100° lost at 180°.
·0112 of H_2O = 4·36 p. c.
IV. ·3657 of substance dried at 100° lost at 150°.
·0150 of H_2O = 4·1 p. c.

The above formula requires 34·08 p. c. Ba, and a loss of 4·4 p. c. water.

When freshly prepared, baric anthraflavate contains a still much larger quantity of water of crystallisation, which it gives up very readily when placed under a bell-jar with sulphuric acid, and to some extent even in the air. In one experiment an air-dried specimen lost 18·2 p. c. when heated to 100°. The formula $2C_{14}H_6BaO_4.3H_2O.10aq.$ would require a loss of 18·3 p. c. for 10aq. This is therefore probably the formula of the freshly crystallised salt.

From these results it appears that anthraflavic acid is an isomer of alizarin. Its origin is not very clear at present, especially as it

appears that it can be produced in variable quantities in the preparation of alizarin according to the mode of experimenting.

I am at present engaged in the study of another secondary product accompanying artificial alizarin, which, unlike anthraflavic acid, possesses dyeing properties, and hope shortly to bring my results before the Society.

XXVIII.—COMMUNICATIONS FROM THE LABORATORY OF THE LONDON INSTITUTION.

No. II.—*On the Action of Nitric Acid on the Dichlorophenolsulphonic Acids.*

By Henry E. Armstrong.

Dichlorophenolparasulphonic Acid, $C_6H_2Cl_2.OH.SO_3H$.—The potassic salt of this acid was prepared by Kolbe and Gauhe's* excellent method, which consists in the addition, with constant stirring, in an open porcelain dish, of 22 parts ordinary concentrated hydrochloric acid to an intimate mixture of 3 parts potassic chlorate and 10 parts potassic phenolparasulphonate, obtained by heating phenol and concentrated sulphuric acid together in equivalent quantities for about six hours at 100°, and subsequent conversion into the potassic salt in the ordinary manner. Violent reaction ensues, which rapidly subsides, and on cooling almost a solid mass is formed. The product, after separation from the excess of acid by draining on a vacuum-filter, dissolves readily in hot water, leaving but a slight residue, a mixture of tri- and tetrachloroquinone. By two or three recrystallisations, the potassic salt may be obtained free from potassium chloride, but for the purpose of most of the present experiments, a crude salt was used from which the chloride had only been partially removed, and for some even the crude product was simply freed from the excess of hydrochloric acid by draining. A very pure salt is most easily obtained by employing a large excess of hydrochloric acid (40 parts); the potassic salt being readily soluble in this medium, whereas potassium chloride is almost insoluble; the latter may be readily separated by filtration, and the former then obtained by concentrating the filtrate. It has been noticed that, on evaporating down the acid mother-liquors, these invariably become almost black and evolve an unbearable odour of (?) dichlorophenol. In all probability dichlorophenolparasulphonic acid

* Ann. Ch. Pharm., cxlvii, 176.

when heated with hydrochloric acid under pressure, is resolved into dichlorophenol and sulphuric acid.

On adding the above salt to nitric acid, sp. gr. 1·36, in considerable excess, 50 grms. dry salt and 200 grms. acid, gradual solution took place, accompanied by a considerable evolution of heat; but little gas was evolved. The temperature was not allowed to exceed 60°. The amount of nitro-product gradually separating out became so large, that finally almost a solid mass was obtained. A quantity of cold water was then added, and the product separated by filtration; on heating the filtrate to the boiling point and allowing it to cool again, a further, not inconsiderable, quantity of the same nitro-body was obtained in the form of crystalline scales. The total product, after well washing on a vacuum-filter, was converted into potassium salt, which, on careful examination by fractional crystallisation, proved to be perfectly homogeneous, and not a mixture of isomeric salts; after purification and recrystallisation it was obtained in the form of groups of short, fine, pale yellow needles, readily soluble in hot, but difficultly in cold water. A portion was decomposed by dilute nitric acid, and the nitro-body recrystallised from a large quantity of boiling water; it was thus obtained in the form of glistening *pale* yellow scales, which under the microscope are resolved into starlike groups of irregular, flat, pointed needles. It is slightly volatile in a current of steam; moderately soluble in boiling water, but nearly insoluble in cold water; melting point, 110° —111°. A chlorine determination showed it to be a *dinitrochlorophenol*, $C_6H_2(NO_2)_2ClOH$.

·1487 grm. gave ·0933 grm. AgCl, or 16·02 per cent. chlorine. The formula, $C_6H_2(NO_2)_2ClOH$, requires 16·25 per cent. chlorine.

On comparing this body with the known isomeric dinitrochlorophenols, of which there are no fewer than five, it was evident that it was identical with Faust and Saame's* β dinitrochlorophenol, melting at 111°, which they obtained by further nitration of a residue from the preparation of chloronitrophenol—by chlorination of the volatile modification of mononitrophenol—remaining after distilling off the latter in a current of steam. They had but a small quantity however, and only prepared and analysed the ammonium, barium, and silver salts; but their description of these tallies in every respect with the same derivatives from my product. Besides these, I have prepared a number of other metallic derivatives, mostly by the action of the respective carbonates on the free phenol; they are all very soluble in hot, but difficultly soluble in cold water. The water of crystallisation was always determined on the air-dried substance.

Potassium derivative, $C_6H_2(NO_2)_2$ ClOK + aq.—Crystallises from hot water in groups of short, fine, brilliant yellow needles.

* Ann. Chem. Pharm. Suppl. Bd., vii, 196.

·659 grm. lost on drying at 120° ·044 grm. H_2O.
·1952 grm. thus dried gave ·066 grm. K_2SO_4.

	Theory.	I.
K	15·21	15·1
H_2O	6·5	6·6

Sodium derivative, $C_6H_2(NO_2)_2ClONa + 1\frac{1}{2}$ aq.—Separates from a hot concentrated solution in tufts of short yellow needles.

·861 grm. lost ·089 grm. H_2O at 100°.
1·2785 grm. ,, ·131 grm. H_2O ,,
·558 grm. thus dried gave ·165 grm. Na_2SO_4.

	Theory.	I.	II.
Na	9·56	9·57	—
$1\frac{1}{2}H_2O$.....	10·09	10·3	10·2

Ammonium derivative, $C_6H_2(NO_2)_2ClONH_4 + 1\frac{1}{2}$ aq.—Groups of short, fine, pale yellow needles. This derivative is chiefly remarkable on account of its extreme insolubility in cold water. On the addition of ammonia even to a dilute solution of any of the metallic derivatives of this phenol, it at once crystallises out.

·8862 grm. lost at 100° ·0934 grm. H_2O.
·8320 grm. ,, ·0885 grm. H_2O.

	Theory.	I.	II.
$1\frac{1}{2}H_2O$	10·28	10·5	10·6

Faust and Saame calculate, from the results of a combustion, that this derivative contains only one molecule of water of crystallisation. I believe that the above direct determination is not too high, since the loss suffered on further heating for some hours at 100° is very slight.

Barium derivative, $\left.\begin{matrix}C_6H_2(NO_2)_2ClO\\C_6H_2(NO_2)_2ClO\end{matrix}\right\}$ Ba + $9\frac{1}{2}$ aq.—Groups of fine, golden-yellow, glistening, prismatic needles. These lose their lustre when exposed to the air. Dried at 150° it becomes vermilion red.

·5384 grm. lost at 150° ·1248 grm. H_2O.
1·2115 grm. ,, ·2789 grm. ,,
·4605 grm. gave ·1877 grm. $BaSO_4$.
·2475 grm. ,, ·1010 grm. ,,

	Theory.	I.	II.
Ba	23·95	23·87	23·9
$9\frac{1}{2}H_2O$.....	23·01	23·02	23·1

Faust and Saame give 9 aq., which corresponds to 22·07 per cent., but I have repeatedly observed a loss on drying of 23 per cent., with substances from various preparations.

Calcium derivative, $\left.\begin{matrix}C_6H_2(NO_2)_2ClO\\C_5H_2(NO_2)_2ClO\end{matrix}\right\}Ca + 7$ aq.—Crystallises from hot water in long, brilliant, flat, pointed, golden-yellow needles. This is at the same time one of the most beautiful and most characteristic derivatives of this phenol.

1·0054 grm. lost at 140° ·2102 grm. H_2O.
·8668 grm. ,, 160° ·181 grm. H_2O.
·2396 grm. gave ·066 grm. $CaSO_4$.
·4134 grm. ,, ·1137 ,,

	Theory.	I.	II.
Ca	8·42	8·1	8·08
$7H_2O$....	20·9	20·90	20·88

Magnesium derivative, $\left.\begin{matrix}C_6H_2(NO_2)_2ClO\\O_6H_2(NO_2)_2ClO\end{matrix}\right\}Mg + 7—10$ aq.—Groups of long, hair-fine, pointed, pale-yellow needles. Exposed to the air these lose their lustre, and when anhydrous are of a dull brick-red colour. The amount of water of crystallisation in this salt is, it would seem, dependent on the degree of concentration of the solution from which it separates; what may be termed the average salt contained an amount corresponding to 7 molecules; twice salts containing 10 molecules were obtained, and frequently others, intermediate in composition between these.

·4766 grm. dry substance gave ·1238 grm. $MgSO_4$.

	Theory.	I.
Mg	5·22	5·19

Copper Derivative, $\left.\begin{matrix}C_6H_2(NO_2)_2ClO\\C_6H_2(NO_2)_2ClO\end{matrix}\right\}Cu + 8$ aq.—Long, hair-fine, branched, silky needles, of a yellowish-green colour. On drying, these become dark brown, but regain their original colour when exposed to moist air.

·2948 grm. lost at 130° ·0658 grm. H_2O.
·8608 grm. air-dry substance gave ·1055 grm. CuO.

	Theory.	I.
Cu	9·88	9·78
$8H_2O$.....	22·4	22·3

It is thus evident that, by the action of nitric acid in excess, and at a somewhat elevated temperature, on dichlorophenol-sulphonic acid, not only is the SO_3H group displaced and the NO_2 group introduced, but one of the chlorine-atoms is also simultaneously replaced by NO_2, giving rise to a dinitromonochlorophenol. It now became of importance to ascertain what would be the result if the reaction were

carried on (I) at a lower temperature; (II) with weaker acid; as it was highly probable that under these conditions both chlorine-atoms would remain unaffected.

I. Potassic dichlorophenolparasulphonate was added in small portions at a time to well-cooled nitric acid (1·36), the proportion of acid to salt being about two to one. The mixture was frequently shaken, but care was taken that the temperature did not rise above 5°. After standing for about two hours, in consequence of the separation of much nitro-product, the whole had solidified; it was then mixed with cold water and the nitro-product separated by filtration and well washed. On boiling the filtrate and allowing it to cool, a considerable quantity of the above-described dinitrochlorophenol was obtained. The solid nitro-body was treated with potassic carbonate-solution, and the mixture of potassium salts separated by fractional crystallisation. Three different products were thus obtained:—α. A relatively small quantity of the potassium derivative of the above-described dinitrochlorophenol. β. This formed about two-thirds of the total product, and consisted of short, yellowish-brown, brittle needles. γ. The third product was an orange-coloured salt, which, when examined under the microscope, was seen to consist of well-formed hexagonal plates.

β. The above-mentioned yellow-brown potassium-derivative yielded, on decomposition with dilute nitric acid, an almost colourless nitro-body, difficultly soluble in boiling water, from which it crystallises out on cooling in long, fine, almost colourless needles, not perceptibly volatile in a current of steam; melting-point 125°; but it was observed to decompose at the moment of fusing. It was at once apparent that this product was identical with Seifart's* orthonitrodichlorophenol, $C_6H_2NO_2Cl_2OH$, obtained by the action of chlorine on orthonitrophenol, and a further comparison of the salts established this.

·2345 grm. gave ·3196 grm. AgCl.
·181 grm. gave ·2458 grm. AgCl.

	Theory.	I.	II.
Cl.....	34·13	33·71	33·6

Sodium Derivative, $C_6H_2NO_2Cl_2ONa + 5aq$.—Glistening yellow needles, very soluble in hot, moderately soluble in cold water.

1·1153 grm. lost at 120° ·313 grm. H_2O.
·3821 grm. lost at 120° ·106 grm. H_2O.
·3465 grm. gave ·1074 grm. Na_2SO_4.

	Theory.	I.	II.
Na.....	10·0	10·03	—
$5H_2O$	28·12	28·06	27·7

* Ann. Ch. Pharm. Suppl. Bd., vii, 198.

Barium Derivative, $\left.\begin{matrix}C_6H_2NO_2Cl_2O\\C_6H_2NO_2Cl_2O\end{matrix}\right\}Ba + 4aq.$—Light red, flat, prismatic needles, very soluble in hot, difficultly soluble in cold water. By slow evaporation of a dilute solution it was once obtained in long, branched, irregular, pale-yellow needles, but on warming under water these were at once converted into the red crystals.

·3642 grm. lost at 160° ·0927 grm. H_2O.

·585 grm. gave ·2435 grm. $BaSO_4$.

	Theory.	I.
Ba	24·86	24·3
$4H_2O$.....	11·55	10·72

Calcium Derivative $\left.\begin{matrix}C_6H_2NO_2Cl_2O\\C_6H_2NO_2Cl_2O\end{matrix}\right\}Ca + 9aq.$—Long, glistening, golden-yellow needles; when exposed to dry air these readily lose water.

·6635 grm. lost at 160° ·1685 grm. H_2O.

·6208 grm. lost at 160° ·1564 grm. H_2O.

	Theory.	I.	II.
$9H_2O$	26·3	25·4	25·2

γ. On addition of dilute nitric acid to a warm solution of the above-mentioned orange-coloured salt, no immediate separation took place, but on cooling it almost solidified to a mass of tufts of pale-yellow, silky needles. These crystals were found to contain potassium, whence it became evident that the orange-salt was the neutral potassium salt, and the pale-yellow needles the acid salt of a nitrosulpho acid. Analysis proved the body to be a nitrochlorophenolsulphonic acid.

Dipotassium Derivative, $C_6H_2NO_2ClOKSO_3K$.—This salt is anhydrous; it is extremely soluble in hot water, moderately in cold.

·6682 grm. gave ·3596 grm. K_2SO_4.

·2955 grm. gave ·1298 grm. AgCl.

	Theory.	I.
K_2	23·67	24·23
Cl	10·70	10·80

Potassium Derivative, $C_6H_2NO_2ClOHSO_3K + \frac{1}{2}aq.$—Pale yellow, arborescent tufts of silky needles, very soluble in warm water, slightly soluble in cold.

·6400 grm. lost at 150° ·0243 grm. H_2O.

1·0349 grm. lost ·0393 grm. H_2O.

·314 grm. gave ·0886 grm. K_2SO_4.

·7277 grm. gave ·2049 grm. K_2SO_4.

·156 grm. gave ·08065 grm. AgCl and ·1200 grm. $BaSO_4$.

	Theory.	I.	II.
K.....	13·4	12·61	12·72
Cl.....	12·18	12·7	—
S	10·9	10·56	—
$\frac{1}{2}H_2O$	2·97	3·8	3·79

It is thus proved that by the action of nitric acid in the cold, two reactions take place simultaneously; the primary reaction consisting in the introduction of the NO_2 group and displacement of the SO_3H group, thus giving rise to nitrodichlorophenol; whilst, as secondary reaction, we have the simple replacement of one chlorine-atom in the dichlorophenolsulphonic acid by NO_2. The small quantity of dinitrochlorophenol formed is, no doubt, a product of the further action of the nitric acid, either on the nitrodichlorophenol, or on the nitrochlorosulpho-acid.

A series of experiments was now instituted on the action of dilute nitric acid at various temperatures, a saturated solution of potassic dichlorophenolparasulphonate being employed. It was found that if to this in the cold a quantity of nitric acid (1·36), about equal in weight to the potassium-salt present, was added, reaction took place accompanied by a considerable evolution of heat, and a nitro-product separated out which proved to be almost pure *orthonitrodichlorophenol.* The filtrate, after heating to the boiling point, gave, as usual, a quantity of dinitrochlorophenol. On adding the nitric acid to the solution previously heated to 50°—60°, a further rise of temperature was observed, and the nitro-product was a mixture of orthonitrodichloro- and dinitrochlorophenol, the filtrate yielding a further quantity of the latter. Finally, if the mixture, after the addition of the nitric acid, was heated to the boiling point, the product consisted almost entirely of dinitrochlorophenol. It is, therefore, possible to prepare at will either of the above in any required quantity. If the mononitrobody is to be prepared, the nitric acid is added to a concentrated solution of the potassium salt previously gently warmed, and the product purified by crystallisation of the potassium salt. On the other hand, to obtain the dinitroproduct, it is best to add the potassium salt gradually to a large excess of nitric acid (1·36), care being taken, however, that the temperature does not rise much above 50°—60°.

Dichlorophenolmetasulphonic Acid.—Kekulé has shown that when phenol is acted on at ordinary temperatures by sulphuric acid, the product is a mixture of two isomeric acids—phenolpara- and phenolmeta-sulphonic acids—which may be separated by fractional crystallisation of the potassium salts. I prepared a quantity of the mixed acids and roughly separated them by crystallisation of the potassium salts. The product so obtained—still a mixture—was treated with potassic chlorate and hydrochloric acids in the proportions mentioned

at the beginning of this paper. The separation of the dichlorometa-salt, which was no doubt formed, from the dichloropara-salt was not attempted, but the product was at once acted on by nitric acid in excess, and the nitro-body formed converted into potassium salt and fractionally crystallised. In this way three products were obtained; 1, the potassium salt of the above-described dinitrochlorophenol; 2, the potassium salt of orthonitrodichlorophenol; 3, a brilliant red potassium salt. To obtain the latter pure, the mother-liquor remaining after the separation of salts 1 and 2, both of which are but slightly soluble in cold water, was decomposed by dilute nitric acid and the product distilled in a current of steam. The body passing over was again converted into the potassium salt, which was then recrystallised. Decomposed with dilute nitric acid, it yields nitrodichlorophenol in the form of a yellow crystalline powder, scarcely soluble in water, which melts at 121°—122°, but sublimes readily below this temperature, and is identical with the body obtained by Fischer* by nitration of dichlorophenol, and by Schmidt and Glutz† by chlorination of nitrophenolparasulphonic acid.

Potassium Derivative, $C_6H_2NO_2Cl_2OK$.—Long, flat, glistening, pointed needles of a brilliant deep-red colour, much resembling that of chromic anhydride, and having, by reflected light, a magnificent metallic green lustre. Very soluble in hot, and to a moderate extent in cold water.

·437 grm. substance gave ·1534 grm. K_2SO_4.

·133 grm. substance gave ·1524 grm. AgCl.

	Theory.	I.
K.....	15·85	15·75
Cl	28·86	28·35

Barium Derivative, $\left.\begin{matrix}C_6H_2NO_2Cl_2O\\C_6H_2NO_2Cl_2O\end{matrix}\right\}Ba + 2aq$.—Bundles of reddish-orange, short, hair-fine needles, very difficultly soluble in water.

1·0994 grm. substance lost at 170° ·0604 grm, H_2O.

·3732 grm. so dried gave ·152 grm. $BaSO_4$.

	Theory.	I.
Ba.....	23·34	23·94
$2H_2O$	6·13	5·4

I believe there is little doubt that the above nitrodichlorophenol, which was obtained in considerable quantity, is the sole product of the action of nitric acid on dichlorophenolmetasulphonic acid; no corresponding dinitrochlorophenol was obtained; and, also, all attempts

* Ann. Ch. Pharm. Suppl. Bd., vii, 180.

† Deut Chem. Ges. Ber., ii, 52.

to convert the dichloromononitrophenol into a dinitromonochlorophenol were unsuccessful; dilute nitric acid was without action, whilst concentrated acid decomposed it entirely. Fischer also only noticed the formation of this one body on nitrating dichlorophenol. The preparation of pure phenolmeta-sulphonic acid being attended with considerable difficulty, I have not yet submitted it alone to the action of nitric acid in support of the above view.

Nitrochlorophenolsulphonic Acid.

On gently warming the above-described acid potassic salt, or even its aqueous solution, with nitric acid (1·36), it is readily converted into *dinitrochlorophenol* melting at 110°—111°.

By the action of chlorine on a cold aqueous solution, *nitrodichlorophenol* is formed, which separates out in the form of a yellow powder. The product was first distilled in a current of steam, and then converted into potassium salt. The salt thus obtained crystallises in flat, pointed, deep red, dichroic needles, not to be distinguished from the same salt of the nitrodichlorophenol obtained by nitration of dichlorophenol. The phenol obtained on decomposing it by dilute acid melted at 122°—123°; that from dichlorophenol at 121°—122°. I am therefore inclined to consider the two as identical.

Potassium Derivative, $C_6H_2NO_2Cl_2OK$.—The air-dry salt is anhydrous.

·3551 grm. gave ·1251 grm. K_2SO_4.
·2023 grm. gave ·2356 grm. AgCl.

	Theory.	I.
K.....	15·84	15·81
Cl_2	28·86	28·81

Action of Nitric Acid on Orthonitrodichlorophenol.

Inasmuch as by the action of nitric acid at a low temperature, and in not too great an excess, on dichlorophenolparasulphonic acid, mononitrodichlorophenol was formed, whereas dinitromonochlorophenol was obtained when a considerable excess of acid and a higher temperature were employed, it was to be expected that the mononitro- would be convertible into the di-nitrocompound. For a long time all experiments to effect this conversion were unsuccessful. Mononitrodichlorphenol was found to dissolve readily in warm nitric acid (1·36), but on subsequent addition of water, it separated out unchanged; with acid of 1·45 sp. gr. a like result was obtained, only that in this case a considerable portion was entirely decomposed, with evolution of red fumes; fuming acid, sp. gr. 1·5, caused this decomposition even more

readily. On digesting for some hours, at the ordinary temperature, with a mixture of fuming nitric and sulphuric acids, and subsequently diluting largely with water, a small quantity of a resinous body was secured, from which, by distillation in a current of steam, long yellow needles were obtained, melting at 120°. These dissolved readily in ammonia, forming a solution which rapidly became brown, and from which acetic acid threw down a brown humus-like matter. A chlorine determination gave following results:—

·075 dry substance gave ·11816 AgCl, equivalent to 38·97 per cent. chlorine.

I have no doubt that this body is *dichloroquinone*, $C_6H_2Cl_2O_2$, which requires 40·12 per cent. chlorine. Faust* obtained this compound by oxidation of trichlorophenol by nitric acid; he gives 120° as the melting-point.

The conversion was, however, finally realised in the following manner:—To a saturated boiling solution of nitrodichlorophenol, a small quantity of nitric acid (1·45) was added, and the solution boiled for 2—3 minutes, then cooled by immersing the vessel in cold water; a crystalline mass gradually separated out, which was recognised as dinitrochlorophenol, melting-point 110°—111°, with all its characteristic properties.

Decomposition of Orthonitrodichlorophenol by Heat.

As above mentioned, this body is decomposed at the moment of fusion; the fused substance assumes a yellow-red colour, and gas is seen to be evolved. In order to examine the gas, I introduced a portion of the dry substance into a tube, which was then drawn off, connected with the Sprengel pump, and exhausted. The lower part of the tube was then heated to about 130° in a bath of sulphuric acid; as the gas was evolved, water was seen to condense in the cool portion of the tube, and later on, long yellow needles. At the conclusion of the experiment, a black, resinous, friable mass remained, insoluble in water and alkalies, slightly soluble in alcohol. The gas was analysed, with the following results:—

Total volume 49·639 c.c., containing—

Nitrogen.....	·685 c.c., or 1·4 per cent
Nitric oxide	48·954 c.c., or 98·6 per cent.

I was inclined to expect decomposition according to the equation—

$$2C_6H_2NO_2Cl_2OH = \underset{\text{Dichloroquinone.}}{2C_6H_2Cl_2O_2} + H_2O + N + NO.$$

* Ann. Ch. Pharm., cxlix, 153.

The composition of the above gas, however, does not verify this. I hope shortly to have sufficient material to investigate this interesting decomposition quantitatively.

A detailed discussion of the constitution of the nitrochlorophenols has lately been published by Petersen,* who theorising, I fear, in many instances on somewhat slight experimental evidence, has constructed "position formulæ" for all the known nitrochlorophenols. He adopts the now probably almost universal view that isomerism in the aromatic series is a consequence of the varying relative positions of the various substituting elements, or groups of elements, in the molecule. I propose for the present simply to apply his argument to the above detailed experiments, and to show in how far they justify his conclusions.

He assumes for nitrodichlorophenol (melting point 125°) and dinitrochlorophenol (melting point 110°—111°), the two bodies which I obtained by nitration of dichlorophenolparasulphonic acid respectively, the constitution—

		1.	2.	3.	4.	5.	6.
(α-Ortho)nitrodichlorophenol....	C_6	OH	NO_2	Cl	Cl	H	H
(α-Ortho)chlorodinitrophenol....	C_6	OH	Cl	H	H	NO_2	NO_2.

The above experiments prove, I believe indisputably, that orthonitrodichlorophenol cannot have the constitution assigned to it by Petersen. That the nitro-group occupies the ortho (2) position would seem proved—to those who believe in the position theory—by its formation from orthonitrophenol (Seifart). Further evidence in favour of this view would probably be considered as afforded by its conversion into dichloroquinone, and also by the readiness with which it is decomposed on heating, with evolution of nitric oxide.

Kekulé, however, has shown that the sulpho-acid from phenol (on heating), is a para (4) compound, since it yields resorcin on fusion with potassic hydrate; it is clear, therefore, that the dichloro-acid derived from this cannot contain either of the chlorine atoms in the para (4) position, that is, supposing no molecular re-arrangement to have taken place: consequently the nitrodichlorophenol formed by treating this with nitric acid cannot contain chlorine in the para position, as it does according to Petersen's formula.

The subject is one of such complication, however, that an enormous amount of investigation will be necessary before the relations of the various nitrochlorophenols are definitely established; until then speculation is useless.

Further experiments in this direction I hope shortly to have the honour of bringing before the Society.

* Ann. Ch. Pharm., clvii, 171, and this Journal, ix, 248.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

A Law in Chemical Dynamics. By J. H. Gladstone and Alfred Tribe.*

It frequently happens that when a more positive metal is immersed in a solution of a less positive one, the former displaces the latter. The authors have investigated the rate at which such displacements take place, when the amount of salt in the same volume of solution is increased by successive multiples, and also the phenomena with which they are accompanied.

These reactions were found peculiarly adapted to the aforesaid purpose, in consequence of (1) their capability of being started and ended at any required moment; (2) their non-interference with, for some time, by the products arising from the respective chemical actions; (3) their uniform rate for periods sufficiently long to enable accurate determinations to be made.

The following table exhibits some of the results obtained with copper and silver nitrate. The duration of each experiment was 10 minutes. The first in the series represents 0·3541 gram of silver nitrate in 100 c.c. of solution, the others being multiples thereof:—

Nitrate-of-silver solution.	Copper dissolved.		Theoretical.	Difference.
Proportional number.	Actual weights.	Average.		
1	0·0045, 0·0050	0·00475	0·00455	+ 0·0002
2	0·0135, 0·0140	0·01375	0·01365	+ 0·0001
3	0·0240, 0·0250	0·0245	0·0259	− 0·0014
4	0·0420	0·0420	0·0409	+ 0·0011
5	0·0600	0·0600	0·0583	+ 0·0017
6	0·0785	0·0785	0·0790	− 0·0005
7	0·0975	0·0975	0·0994	− 0·0019
8	0·1230, 0·1230	0·1230	0·1228	+ 0·0002
9	0·1510, 0·1480	0·1495	0·1481	+ 0·0014
10	0·1680, 0·1670	0·1675	0·1749	− 0·0074
11	0·1955	0·1955	0·2035	− 0·0080
12	0·2170, 0.2285, 0·2310, 0·2200	0·2241	0·2336	− 0·0095
14	0·2740	0·2740	0·2982	− 0·0242
16	0·3270	0·3270		
20	0·4540, 0·4100	0·4320		

* Proc. Roy. Soc., xix, 498.

The actual weights corresponding to 1, 2, 3, 4, and 5, multiplied by 3, give, within the limits of experimental error, those of 2, 4, 6, 8, and 10; *i.e.*, *in a given time, twice the quantity of silver salt gives three times the chemical action.* The close agreement of the observed numbers with those calculated on this supposition, as far as the 9th term, is shown in the 4th and 5th columns. The law then breaks down, and after about 7 per cent. the increased action is almost in direct ratio with the increased strength.

When it was perceived that within easily ascertainable limits the chemical action is the same for similar consecutive periods of time, experiments were made in solutions diminishing in strength from the first in the series. It was only necessary to lengthen the time of exposure. It was thus found that the law of three times the chemical action for twice the quantity holds good through at least 11 terms of the powers of 2,—in fact, from a solution that could dissolve 1 grm. of copper during the hour, to a solution that dissolved only 0·000001 grm., a million times less.

The position of the metal in the solution makes no difference to this 2—3 law.

The decrease in the rate at about 3·5 per cent. of salt in solution is not affected by increasing the quantity of liquid.

Similar series of experiments were made with zinc and copper chloride, zinc and copper sulphate, zinc and lead nitrate, iron and copper sulphate, and other combinations; and in every instance where the solution was weak and the action simple, the 2—3 law holds good.

The manner in which the metals were deposited was examined, and the currents produced were studied. In the case of copper and silver nitrate, it was evident that there was not merely a transference of the nitric element from one liquid to the other, but an actual molecular movement of it towards the copper plate, producing an accumulation of nitrate of copper there, and a corresponding loss of salt in the liquid that is drawn within the sphere of chemical action. Hence the upward current of almost pure water, and the downward current of strong solution of copper nitrate; these currents explain, in a great measure, the cause of the uniform rate of this class of actions.

It appeared by experiment that a strong solution of silver nitrate offers less resistance than a weak one; and it was also found, on adding potassium nitrate to the silver nitrate, that its power of attacking the copper plate was increased, that the augmentation of the foreign salt increased the action still further, and that the 2—3 law holds good between two solutions in which both the silver and potassium salt are doubled, though it does not hold good if the quantity of foreign salt be kept constant. Similar results were obtained with mixed nitrates of silver and copper.

While these later experiments offer an explanation of the fact that a solution of double the strength produces more than double the chemical action, they do not explain why it should produce exactly three times the effect, or why the ratio should be the same in all substitutions of this nature hitherto tried.

A. T.

Researches on the Density and Expansibility of some Solutions. By C. MARIGNAC.*—Part II.

THE instrument employed in these researches for measuring the expansion was the dilatometer of H. Kopp, *i.e.*, large sized thermometers having bulbs of from 15 to 28 cub. cent. capacity. The divisions on the stem allowed variations amounting to no more than $\frac{1}{140000}$ of the total volume to be read off. The experiments were confined to aqueous solutions. The tubes of the dilatometer were kept closed during an experiment by long thin india-rubber tubes furnished with stoppers. The author could detect no perceptible variation in the volume of a solution, when kept at a constant temperature during several days, the first observation being made as soon as possible after the solution was prepared.

The following tables give the densities, molecular volumes, and co-efficient of expansion, at 20°, of various aqueous solutions.† Column n gives the number of molecules of water present; D the density of the solution; W, its molecular weight; V, its molecular volume (water = 18); $V-18n$, the difference between the molecular volume of the solution and that of the water which it contains; E, the co-efficient of expansion; all at 20°.

Sulphuric Acid, $H_2SO_4 + n$ Aq.

n.	D.	W.	V.	$V-18n$	E.
0	1·83211	98	53·40	53·40	0·0005585
5	1·41317	188	132·80	42·80	0·0005660
10	1·26099	278	220·08	40·08	0·0005845
15	1·19033	368	308·60	38·60	0·0005697
25	1·12292	548	487·14	37·14	0·0004975
50	1·06451	998	935·9	35·9	0·0003867
100	1·03251	1898	1835·0	35·0	0·0003107
200	1·01592	3698	3633·6	33·6	0·0002602
400	1·00728	7298	7232·8	32·8	0·0002339
Water	0·99826	18	18	—	—

* Ann. Ch. Phys. [4], xxii, 415—444.

† The original paper gives also the interpolation formulæ (to the second power of the temperature), by which these results are calculated, and the experimental data on which they are founded.

The continued decrease of the numbers in the last column show that, whether sulphuric acid itself be mixed with water, or a dilute sulphuric acid be still further diluted, contraction is always the result.

Sodium Sulphate, $Na_2SO_4 + n$ Aq.

n.	D.	W.	V.	V−18*n*	E.
25	1·23443	592	478·7	28·7	0·0004102
50	1·12645	1042	923·4	23·4	0·0003608
100	1·06545	1942	1819·5	19·5	0·0003051
200	1·03287	3742	3616·6	16·6	0·0002599
400	1·01586	7342	7214·8	14·8	0·0002344

This table shows that contraction takes place when a solution of sulphate sodium is diluted with water.

Acid Sodium Sulphate, $NaHSO_4 + n$ Aq.

n.	D.	W.	V.	V−18*n*.	E.
25	1·17053	570	486·1	36·1	0·0005554
50	1·09168	1020	932·7	32·7	0·0004349
100	1·04718	1920	1830·3	30·3	0·0003390
200	1·02357	3720	3628·0	28·0	0·0002776

Comparative Table of the Molecular Volume of solutions of Neutral Sodium Sulphate, Acid Sodium Sulphate, and Sulphuric Acid.

n.	H_2SO_4.	$\left.\begin{matrix}Na\\H\end{matrix}\right\}SO_4$	Na_2SO_4.
25	487·1	486·1	478·7
50	935·9	932·7	923·4
100	1835·0	1830·3	1819·5
200	3633·6	3628·0	3616·6
400	7232·8	—	7214·8

It will be seen that the molecular volume of the acid sulphate is always above that of the mean of the sulphuric acid and neutral sulphate; so that when a solution of neutral sulphate is mixed with sulphuric acid, expansion *always* takes place.

Hydrochloric Acid, HCl + n Aq.

n.	D.	W.	V.	V − 18n.	E.
6·25	1·12030	149	132·77	20·27	0·0004546
12·50	1·06700	261·5	244·65	19·65	0·0003460
25	1·03500	486·5	469·23	19·23	0·0002799
50	1·01755	936·5	918·75	18·75	0·0002394
100	1·00815	1836·5	1818·42	18·42	0·0002240
200	1·00330	3636·5	3618·23	18·23	0·0002107

Sodium Chloride, NaCl + nAq.

n.	D.	W.	V.	V − 18n.	E.
12·5	1·15292	283·5	245·47	20·47	0·0004135
25	1·08207	508·5	469·12	19·12	0·0003530
50	1·04227	958·5	918·02	18·02	0·0002960
100	1·02069	1858·5	1817·66	17·66	0·0002532
200	1·00965	3658·5	3617·58	17·58	0·0002305

Sugar, $C_{12}H_{22}O_{11}$ + nAq.

n.	D.	W.	V.	V − 18n.	E.
25	1·19242	792	663·0	213·0	0·0003434
50	1·11506	1242	1111·9	211·9	0·0002985
100	1·06333	2142	2010·9	210·9	0·0002595
200	1·03265	3942	3810·8	210·8	0·0002312
400	1·01594	7542	7410·8	210·8	0·0002118

In conclusion the author points out that the above experiments prove that, in a mixture of a solution with water, the co-efficient of expansion of the mixture is higher than the mean of the co-efficients of expansion of the two constituent liquids. The above results also confirm the general law that the dilution of a solution is attended with contraction. This contraction, however, diminishes as the temperature at which the mixture is made rises, so that it seems very probable that at temperatures sufficiently elevated the dilution of a solution would no longer be accompanied by contraction of volume.

In a note appended to the paper, the author gives the explanation of a curious phenomena observed by him in his research on the heat evolved by the dilution or mixing of saline solutions.* When two concentrated solutions were mixed, and water was added to the mixture, the amount of heat set free apparently differed from that evolved

* Archives, xxxvi, 335; 1869.

when the same concentrated solutions were first separately diluted, to the same extent as before, and then mixed in the diluted state. This apparent discrepancy is stated by the author to be due to the difference existing between the actual specific heat of the solution and that calculated from the specific heat of its component parts. Finally, the author arrives at the conclusion that the state of combination in which a salt is held in solution is invariable, and, moreover, that this state is produced at once and definitely, the moment the mixture is made or the dilution accomplished.

A. D.

New Facts concerning the Communication of Heat. By M. L'ABBÉ LABORDE.*

WHEN the flame of a gas blowpipe is directed almost vertically down upon the surface of water contained in a saucer, the temperature of the water gradually rises, but is with difficulty raised to 80°, and cannot be raised to boiling. The author does not consider that this is due to evaporation. On causing a quantity of water to flow in a fine stream through the blowpipe-flame, the temperature of the water was only raised three degrees.

If the water, instead of flowing in a stream, is allowed to fall as a thin sheet, the point of the flame may be directed against the water without any fear of penetrating the sheet, and the finger may be held at a distance of only a few millimeters in front of the flame, without the slightest danger, if such a sheet of water is interposed. The author deduces from his experiments the following practical rules.—

When it is impossible to get at the focus of a conflagration, it is useless to throw water on the flames, and the water should rather be directed against such objects as are to be protected from the flames. Secondly, if a flame is issuing from an opening, it may be effectually cut off by directing against it, from a suitable nozzle, a sheet of water; the flame would thus be prevented from injuring any neighbouring houses, &c., &c.

A. D.

Thermo-chemical Researches upon the Ammoniacal Salts. By BERTHELOT.†

THE author, having observed in his experiments upon nitrification, that the mixture of solutions of potassium carbonate and ammoniacal salts gave rise to the absorption of a considerable amount of heat, commenced a series of experiments in order to clear up this singu-

* Compt. rend., lxiii, 561—563.

† Compt. rend., lxxiii, 745—749; and 864—868.

lar phenomenon. He proposes to give the results with ammoniacal salts: first, those formed by strong acids, then those with weak acids, and, lastly, the reciprocal action between these salts and the corresponding alkaline salts.

First Part.—Ammoniacal Salts formed by Strong Acids.

Although the heat disengaged during the neutralisation of ammonia by acids had been already measured, the author determined to repeat the experiments, and found that the results were not sensibly affected either by different degrees of dilution or by the presence of excess of ammonia or of the acid. The means of the results obtained were for $HCl + NH_3$ 12·45, for $HNO_3 + NH_3$ 12·57, and for $H_2SO_4 + NH_3$ 14·53. The relative value of the saturation of acids by ammonia may be determined by three indirect methods, first, that of Thomsen (*the reciprocal action of acids and salts*), by acting on each of two salts with the acid contained in the other, the difference of the two thermal effects being equal to the difference of the heats of neutralisation, $K_1 - K = N - N_1$. The author found:—

			$K_1 - K$.	$N - N_1$.
NH_4Cl	$+ H_2SO_4$....	$+ 0·388$	2·044	2·088
$(NH_4)_2SO_4$	$+ HCl$.....	$- 1·656$		

Thomsen gave + 0·32 and − 1·48.

NH_4NO_3	$+ H_2SO_4$....	$+ 0·303$	2·060	1·960
$(NH_4)_2SO_4$	$+ HNO_3$....	$- 1·757$		

The author has also found another method of verification, namely, by acting upon an ammonium salt with potassa, and then on the corresponding potassium salt with ammonia, the thermal difference being equal to the difference of the heat of neutralisation (*reciprocal action of bases on salts*).

			$K_1 - K$.	$N - N_1$.
$(NH_4)_2SO_4$	$+ KHO$ ...	$+ 1·34$	1·48	1·18
K_2SO_4	$+ NH_3$	$- 0·14$		
$(NH_4)_2SO_4$	$+ NaHO$ ..	$+ 1·25$	1·38	1·34
Na_2SO_4	$+ NH_3$	$- 0·13$		
NH_4Cl	$+ KHO$....	$+ 1·34$	1·37	1·14
KCl	$+ NH_3$	$- 0·03$		
NH_4Cl	$+ NaHO$ ..	$+ 1·33$	1·37	1·24
$NaCl$	$+ NH_3$	$- 0·04$		

These calculations are based upon the knowledge of the heat disengaged during the reaction of other bases with the same acids. Another method of verification consists in causing four salts formed by two bases and two acids, to react upon one another in pairs (*the*

reciprocal action of salts); the difference of the two thermal effects $K_1 - K$ is represented by subtracting the difference of the heat of neutralization of the two acids by the one base, from the same difference for the other base—

$$K_1 - K = (N - N_1) - (N' - N'_1).$$

The results obtained by the author correspond with this theorem, and he concludes that these verifications show that each of the values obtained may be regarded as correct within 0·025; and he intends to employ the formula $K_1 - K = (N - N_1) - (N' - N'_1)$ to determine one of the values of N when it cannot be obtained directly with sufficient accuracy.

Second Part. Ammonium Salts formed by the Weak Acids.

I. *Boric Acid.*—When successive quantities of ammonia are added to a solution of boric acid, the disengagement of heat continues even after the addition of the second equivalent of ammonia; and a similar phenomenon is observed in the case of ammonium phenate* and the alkaline alcoholates. The quantity of water present also causes a variation in the result. In neutralising boric acid with soda, however, the disengagement of heat ceases with the second equivalent of the latter, although, in this instance, as with ammonia, the state of dilution exerts a perceptible influence. The following table gives the heat disengaged in the formation of sodium and ammonium borates in presence of various quantities of water:—

	Boric acid and soda.	Boric acid and ammonia.	Difference.
$220H_2O$	11·69	9·44	2·25
$330H_2O$	11·56	8·93	2·63
$440H_2O$	11·13	8·44	2·69
$1320H_2O$	10·91	7·27	3·64

These numbers show that the heat disengaged during the neutralisation of soda and ammonia by boric acid is less than with the strong acids; moreover the difference of the heats of neutralisation of the strong acids by soda and by ammonia is 1·3, and is independent of the quantity of water present, whilst that of boric acid varies from 2·25 to 3·64, according to the amount of water. With the bibasic borates it is even greater, being 4·13.

II. *Carbonic Acid.*—On mixing aqueous solutions of carbonic acid and ammonia in the proportions to produce the neutral carbonate (one equivalent in 20 litres), the author obtained the value 5·35. In order to control this result, the amount of heat disengaged in the formation

* Compt. rend., lxxiii, 673.

of ammonium bicarbonate was first of all determined indirectly, and found to be 9·73 for 2 litres of solution. Another experiment was then made to ascertain the amount of heat further disengaged on neutralising the ammonium bicarbonate by ammonia, which was found to be 2·62: therefore, 9·73 + 2·62 = 12·35, is the heat disengaged for two equivalents of ammonium carbonate, or 6·17 for one equivalent in presence of two litres of water = 110 H_2O. By the indirect method of "the reciprocal action of salts," in presence of 220 H_2O, the values 5·73, 6·00, and 5·83 were obtained, which agree pretty well with 6·17 previously found with liquors of double the strength = 110 H_2O. For ammonium bicarbonate by the same method, the values 9·72, 9·62, 9·70, and 9·83 were obtained, closely corresponding to the number 9·73 previously found. The following table shows the influence exerted by the relative proportions of ammonia, carbonic acid, and water:—

CO_2 +	NH_3	in presence of	$110H_2O$	disengages	9·73
+	$1\frac{1}{3}NH_3$	,, ,,	$146H_2O$	,,	10·94
+	2 NH_3	,, ,,	$220H_2O$	,,	12·34
+	3 NH_3	,, ,,	$330H_2O$	,,	13·24
+	4 NH_3	,, ,,	$440H_2O$	,,	13·62
+	5 NH_3	,, ,,	$550H_2O$	,,	13·92
+	6 NH_3	,, ,,	$660H_2O$	,,	14·04
+	7 NH_3	,, ,,	$770H_2O$	,,	14·07

The author concludes by observing that these and the results previously obtained with phenic acid, show that the proportion of water present exercises a much more marked influence with boric acid than with carbonic acid and phenol, but that the decomposing influence of water seems to produce, at first, greater effects on the compounds of the two latter, which however rapidly becomes very small, whilst with boric acid the progression is more regular.

C. E. G.

On the Amount of Heat Evolved or Absorbed in the Solution of Sodium Phosphate containing different Proportions of Water of Crystallisation. By L. Pfaundler.*

Horstmann, in calculating (from certain determinations by Debray of the vapour-tension of sodium phosphate) the amount of heat evolved by the transformation of Na_2HPO_4 into $Na_2HPO_4 + 7H_2O$ and $Na_2HPO_4 + 12H_2O$, regretted that no direct calorimetrical estimations existed by which the results of his calculations might be verified. The author has accordingly made a series of determinations to supply this want. His method depended on the fact that when equivalent quantities of the three salts are dissolved in an excess of water, the resultant solutions have precisely the same composition; the differences

* Deut. Chem. Ges. Ber., iv, 773—776.

in the calorimetrical effects produced by the transformation of the first salt into the second and third should therefore correspond to those obtained by Horstmann's method of calculation. The first salt was prepared by recrystallisation and drying between filter paper, the third by continued heating to 100°, and the second by heating the first salt until the excess of water over that required by the formula had been driven off. The molecular weights of the three salts are:—

Salt α.	Salt β.	Salt γ.
$Na_2H.PO_4$.	$Na_2HPO_4 + 7H_2O$.	$Na_2HPO_4 + 12H_2O$.
142·8	268·8	358·8

In the experiments the following quantities of the salts were invariably employed; they are in the relation of the above molecular weights:—

Salt α, 6·51 grm. Salt β, 12·25 grm. Salt γ, 16·35 grm.

The water employed for solution amounted to—

294·84 grm. 289·10 grm. 285·00 grm.

These amounts are so calculated that in all the experiments the final weight of liquid (301·35 grams) should be the same, and that it should possess the same composition (5·425 per cent. of salt γ) and the same specific heat. The specific heat of the solution was found to be 0·972. The solutions were effected in a calorimeter of thin brass, fitted with an agitator shaped in the form of a dish. The temperature of the finely powdered salts was as nearly as possible that of the water to which they were added. The solution of salt γ required $1\frac{1}{2}$ minutes, salt β from 2 to 3 minutes. Salt α required always at least 5 minutes for complete solution. The results of the experiments are arranged in the following table:—

No. of Experiment.	Salt used, and calculated water.	Amount of water found.	Total water value of calor. with contents.	Initial temp.	Final temp. (cor.)	Increment of temp.	Heat generated.	Correction for slight difference in temp. of salt.	Corrected value of quantity of heat.	Mean.
1	Salt γ (62·7 p. c.)	62·62	297·48	17·65	14·23	−3·42	−1017·38	−10·46	−1027·84	−1024·9
2				17·65	14·26	−3·39	−1008·84	−11·38	−1020·22	
3				17·94	14·52	−3·42	−1017·31	−8·50	−1025·88	
4				18·49	15·07	−3·42	−1017·38	−8·59	−1025·97	
5	Salt β (50·23 p. c.)	50·37	297·48	18·90	17·17	−1·73	−518·68	..	−518·68	−516·2
6		,,	,,	19·40	17·68	−1·72	−513·76	..	−513·67	
7	Salt α (6·30 p. c.)	6·14	297·48	18·84	19·68	+0·84	+249·88	..	+249·88	+249·8
8		,,	,,	18·86	19·70	+0·84	+249·88	..	+249·88	
9		6·29	,,	17·90	18·65	+0·75	+223·11	..	+223·11	+227·5
10		,,	,,	17·94	18·72	+0·78	+232·03	..	+232·03	

In experiments 9 and 10 the solution required a longer time than usual; the numbers are probably less accurate on this account than the others, and they have, therefore, been excluded from the means. It will be seen that only by the solution of salt α is heat evolved.

The calculation of the heat produced by the transformation of the salt α into the others is made in the following way:—

16·35	grm. salt γ	required on	solution	1024·98	thermal units.
12·25	,, β	,,		516·22	,,
4·10	,, water	require	,,	508·76	,,

The unit weight of water requires, therefore, 124·09 thermal units.

16·35	grm. salt γ	required on	solution	1024·98	thermal units.
6·51	,, α	evolve	,,	249·88	,,
9·84	,, water	require	,,	1274·86	,,

Or the unit weight of water requires 129·56 thermal units.

12·25	grm. salt β	required on	solution	516·22	thermal units.
6·51	,, α	evolve	,,	249·88	,,
5·74	,, water	require	,,	766·10	,,

Or the unit weight of water requires 133·47 thermal units.

These results differ widely from those of Horstmann. The first 7 mols. water evolve per kilo. almost as much heat as the next 5 mols.

	$Na_2HPO_4 + 7H_2O$.	$(Na_2HPO_4 + 7H_2O) + 5H_2O$.	$Na_2HPO_4 + 12H_2O$.
Horstmann..	215·2	78·6	158·3
Pfaundler ..	133·47	124·09	129·56

These differences cannot be due to errors in calorimetrical measurement; possibly they are owing to imperfections in the estimation of the vapour-tensions. T. E. T.

On the most Economical Disposition of Voltaic Batteries with respect to the Size of the Plates. By Th. du Moncel.*

The further researches of the author on the relative sizes of battery-plates confirm his former views. He points out that by diminishing the zinc plate there is a great saving of material, as there is necessarily less local action. S. W.

On the Voltaic Energy of Two-liquid Batteries. By F. Le Blanc.†

The author some years ago undertook these investigations with a view of ascertaining what liquid was most suitable for the electro-positive

* Compt. rend., lxxiii. 906. † Ibid., 904.

plate of a Bunsen's cell. Amongst the substances examined were the following:—Hydrochloric acid, *aqua regia*, hydrochloric acid with manganese dioxide, sulphuric acid with potassium dichromate, chloric acid in solution, and potassium chlorate with dilute sulphuric acid. The results of experiment were quantified by the voltameter, and also by the weight of copper deposited in an electrolysing cell placed in the circuit. It was shown that hydrochloric acid did not add to the voltaic energy; *aqua regia*, and, still better, the mixture of manganese and hydrochloric acid produced powerful effects; the mixture of potassium dichromate and sulphuric acid produced effects inferior to those of the ordinary nitric acid battery, but had the advantage of not emitting noxious fumes; chlorous acid, or the mixture producing it, gave relatively energetic action, increasing with the concentration of the solutions. S. W.

Thermic Researches on Voltaic Energy. By P. A. FAVRE.*

FAVRE'S researches, the results of which appear in this communication, are now extended to the determination of the voltaic energy produced in couples, by permanganic acid, by fuming nitric acid, by hypochlorous acid, as also in a couple where hydrogenized palladium is acted upon by cupric sulphate. For the purposes of these investigations he has determined with greater accuracy than heretofore the voltaic energy of a Smee's couple, eliminating as much as possible all local action, and the consequent partial electrolysis of the zinc sulphate. His method is as follows:—The battery was enclosed in the calorimeter, the external resistance being made to balance the internal. Part of this external resistance consisted of a thermorheostat and a voltameter destined to contain a liquid such as would not be decomposed, should the battery act as two plates of zinc immersed in a solution of a zinc salt. This was effected by placing zinc sulphate in the voltameter. To electrolyse this body, about 66,000 heat-units are required, to produce which amount five cells of Smee are necessary, according to the old determination, so that, if one cell ceased to function as an electromotor, the circuit would be broken. Operating in this manner the thermic equivalent for the voltaic energy of a Smee's element was found to be, in round numbers, 15,000 heat-units, a considerable increase on the older determination. On the basis of this number two series of experiments were instituted. In the first series, A, the calorimeter contained the couple to be examined, a Smee's element, and a sufficiently powerful thermorheostat, joined together by thick, short wires. In the second series, B, the Smee's element and thermorheostat

* Compt. rendus, lxxiii, 890; a continuation of researches published in 1869 (Compt. rend., lxix, 34).

were placed outside the calorimeter, the couple to be examined being placed within.

I. *Couple with Fuming Nitric Acid.*

	A. Heat-units.	B. Heat-units.
Heat registered by the calorimeter for one equivalent of hydrogen set free in each element	72,214	2,867
Heat corresponding to one equivalent of hydrogen set free in the couple under examination and united with the oxygen of the acid	52,714	,,
Heat transmissible to the circuit (voltaic energy)	,,	49,847

Examining the number representing the voltaic energy in conjunction with other numbers obtained in previous researches, it will be seen that the gain is sensibly equal to the amount of heat generated when the fuming acid is diluted with water, for when ordinary concentrated acid is used, the number representing the voltaic energy is 46,447; the difference is then 3,400 in favour of the fuming acid. The fuming acid, when treated with water so as to reduce it to the state of ordinary acid, gives 4,213 heat-units, a number not far removed from that which represents the gain in voltaic energy when fuming nitric acid is used.

If we compare a Grove's element in which fuming nitric acid is employed, with an element in which the zinc is acted upon by dilute nitric acid, the author's views are still further justified. The last-named combination disengages for each equivalent 43,247 heat-units. If to this be added 2,000 heat-units (the difference between the action of dilute nitric acid and equally dilute sulphuric acid on zinc) and also 6,000 heat-units (the heat of hydration of fuming nitric acid), we obtain the number 51,247, not very different from the above mentioned number, 52,714. A series of experiments was entered upon to elucidate this matter. A Smee's couple with normal nitric acid placed inside the calorimeter and connected with a similar element with normal sulphuric acid outside, gave great quantities of heat without any observable production of gas, as long as the circuit remained unclosed. On making the circuit, there was a considerable increase of heat, and the amount of hydrogen released in the couple with nitric acid was equal to that released in the couple with sulphuric acid. Again, when a voltameter with platinum electrodes and a partition had the negative chamber charged with sulphuric acid, and the positive with concentrated nitric acid, everything took place as though the two compart-

ments contained normal sulphuric acid alone. In a third experiment a voltameter was used with a double partition, the middle compartment was filled with nitric acid, and the two external compartments which contained the electrodes were charged with sulphuric acid. The results were exactly the same as when all the three compartments contained sulphuric acid. Multiplying these chambers and placing one of the oxidizing acids under examination in each compartment, sulphuric acid occupying the outer compartments, into which the electrodes were inserted, the same phenomena were exhibited as in the previous case. These results are conformable to the author's ideas of molecular synchronism developed in a former communication.

II. *Couple with Permanganic Acid and Sulphuric Acid mixed.*

The mean voltaic energy may be represented by 39,234 heat-units. There is a notable want of constancy in this arrangement, and in spite of the presence of sulphuric acid an abundant precipitate is formed, which attaches itself to the porous cell.

III. *Couple with Hypochlorous Acid.*

The voltaic energy of this couple is equivalent to 50,806 heat-units. This arrangement surpasses in energy all others examined hitherto.

S. W.

Thermic Researches on Voltaic Energy (continued).
By M. P. A. Favre.*

IV. *Couple with Cupric Sulphate and Occluded Hydrogen.*

In this couple the plate of hydrogen occluded by palladium was immersed in sulphuric acid, and separated by a diaphragm from a plate of platinum in cupric sulphate. As the direct determination of the voltaic energy of this couple presented great difficulties, it was calculated from the results of the experiments in Table I.

Suppose that in the electrolysis of hydrogen sulphate the electrodes used are (1) a palladium plate absorbing hydrogen, and a platinum plate; (2) a palladium plate absorbing hydrogen and a palladium plate with occluded hydrogen, and let the heat borrowed by the voltameter from the battery in these two cases be called a and b respectively. Also, in the electrolysis of cupric sulphate, when the electrodes are—(1) two platinum plates, (2) two copper plates, let the quantities of heat borrowed by the voltameter in these two cases be a' and b' respectively; then it can be shown that the voltaic energy of a cell of the battery is represented by the formula—

$$a - b - (a' - b')$$

* Compt. rend., lxxiii, 936.

TABLE I.

Conditions of the experiments.	Heat indicated by calorimeter, which includes the battery and the thermorheostat.	Heat borrowed by the voltameter for the electrolysis of 1 equivalent of sulphuric acid (calculated).	Heat indicated by the calorimeter, which includes the voltameter, and corresponds to the electrolysis of 1 equivalent of sulphuric acid.	Volume of hydrogen evolved by every couple of Smee's battery in 25 minutes.	Corresponding volume of hydrogen or of oxygen evolved in the voltameter.	Deflections.
		Heat-units.		Heat-units.	c.c.	°
I. Battery and thermorheostat within the calorimeter; the voltameter, Pd—Pt (Pd fixing the H disengaged) without	9800	(A) 47275	..	106·0	47·5 of O	1·35
The arrangement reversed ..	,,	,,	E 18070	102·5	44·0 of O	1·25
II. The cells and thermorheostat within the calorimeter, the voltameter PdH—Pt (Pd fixing the SO_4) without	11151	B 16208	,,	79·0	79·0 of H	0·75
Arrangement reversed	,,	,,	F 8496	71·0	71 0 of H	0·70
III. Two cells and the thermorheostat within the calorimeter, the voltameter (PdH—Pd (fixing the radicals SO_4 and H) without	17182	(C) 4146	,,	148·5	0·0	1·40
The arrangement reversed ..	,,	,,	G 2098	155·0	0·0	1·60
Two cells and voltameter, PdH—Pt, within the calorimeter	16801	D 4908	,,	224·0	224·0 of H	,,
Two cells, thermorheostat and voltameter, PdH—Pd within the calorimeter ..	17984	D 1271	,,	154·0	0·0	,,
Two cells and thermorheostat within the calorimeter, the galvanometer being within the circuit .	19212	,,	,,	173·0	,,	1·70
Two cells and thermorheostat within the calorimeter, the galvanometer not being within the circuit .	19255	,,	,,	172·0	,,	,,

The author draws attention to the fact that a great part of the heat set free in the voltameter is transmissible to the other parts of the circuit when there is no disengagement of gases, whilst it remains confined to the voltameter when gas is evolved, as, for example, hydrogen in (F).

This phenomenon appears to the author to belong to the same class as that observed by him in the electrolysis of hydrobromic and hydri-

odic acid in a non-partitioned voltameter—that no more heat is evolved when the evolution of gas is completely stopped, whilst before this happens a decrease in the evolution of gas is accompanied by an increased evolution of heat.

Some oxidising acids were electrolysed by the current of a Smee's battery, which itself was placed within the calorimeter, whilst the voltameter remained outside. The results are given in Table II.

If from the numbers 46,000 and 48,000 heat-units, which express the heat borrowed from the battery for the electrolysis of normal sulphuric acid, the last five numbers are subtracted, then will the difference, increased by the 15,000 heat-units representing the voltaic energy of a Smee's couple, furnish in every case the voltaic energy of the corresponding couple with two liquids.

TABLE II.

Acids used.	Electrolysis of the different acids.		
	Heat borrowed from the battery.		Heat which remains confined in the non-partitioned voltameter.
	Voltameter not partitioned.	Voltameter partitioned with sulphuric acid in the positive compartment.	
	Heat-units.	Heat-units.	Heat-units.
Boiled sulphuric acid	59125	55160	26455
Normal sulphuric acid	46110	48102	13664
Normal nitric acid	45933	50000	15467
Diluted mixture of sulphuric acid and chromic acid	29721	28824	28875
Dilute mixture of sulphuric acid and permanganic acid	18383	17696	23634
Fuming nitric acid (HNO_3, 0·944HO) (1)	8178 A	15354 B	9956
Concentrated nitric acid (HNO_3.6·820HO) (1)	14214 A	18810 B	9950
Hypochlorous acid	5246 A	11092 B	8378

The numbers calculated from this table are contained in Table III, from which it can also be seen how far they agree with those obtained by direct determinations.

TABLE III.

Acids used.	Voltaic energy found by direct determination.	Voltaic energy calculated from the number of thermal units borrowed by the acid in the non-partitioned voltameter.	Voltaic energy calculated from the number of thermal units borrowed by the acid in the partitioned voltameter.
	Heat-units.	Heat-units.	Heat-units.
Chromic acid	30225	31279	34176
Permanganic acid	39234	42617	45304
Fuming nitric acid	49848	52822	47646
Concentrated nitric acid..	46447	46786	44190
Hypochlorous acid	50807	55754	51908

The author attributes the differences between the results of experiment and of calculation to unavoidable errors of experiment. The experiments on the electrolysis of permanganic acid render it probable that the inconstancy of every element in which permanganic acid is used as one liquid is due to the gradual reduction of the acid, and that the energy of these elements would be considerably greater if the oxygen furnished by the permanganic acid did nothing but oxidise the hydrogen set free by the electrolysis of the sulphuric acid.

In the electrolysis of hypochlorous acid, it was observed that for 315 c.c. of hydrogen evolved in the cell, and consequently burned within the voltameter by the hypochlorous acid, there are set free 544 c.c. of chlorine and 116 c.c. of oxygen in the voltameter. Now, if the hydrogen had been burned by the oxygen of the hypochlorous acid, the volume of the chlorine set free in the voltameter would be nearly equal to the volume of hydrogen evolved in one cell; but as the volume of the liberated chlorine is much greater, it must be supposed that the hydrogen is almost completely burned by the chlorine, with formation of hydrochloric acid, which, acting upon the hypochlorous acid, gives rise to the evolution of a volume of chlorine twice as great as that of the hydrogen evolved in one cell.

The author then draws attention to the fact that although the normal acid has a much greater electrolytical resistance, the heat borrowed in electrolysis from the battery is very much greater in the case of the boiled acid, and concludes that the boiled acid must offer a very much greater physical resistance to the current than the normal acid, a conclusion confirmed by several other observations.

R. S.

On some Electrocapillary (Chemosmotic) Phenomena. By O. LOEW.*

WHEN potassium sulphide and cupric sulphate are separated by a membrane, metallic copper is precipitated instead of cupric sulphide. For this and similar phenomena the term electrocapillarity was introduced by Becquerel, who considers that in this and in analogous phenomena electrical currents are at work. The author thinks that they may be explained without reference to electricity, and proposes the name *chemosmose*. When a moderately sized crystal of cupric sulphate is immersed in a concentrated solution of potassium sulphide contained in a test-tube, the formation of a black crust of cupric sulphide is observed, and soon after a dark yellow coloration is seen to ascend from the crystals, indicating the formation of potassium disulphide. After twelve hours' standing, the black lump formed at the bottom, under the crust of cupric sulphide, is found to consist of metallic copper. Silver nitrate furnishes, under the same conditions, only a small quantity of metallic silver, whilst by far the greater part of the salt is not acted upon at all.

Crystals of cupric sulphate covered with a concentrated solution of potassium hydrate yield a loose mixture of the black oxide and the hydrate of copper, and a blue solution of cupric oxide in potassium hydrate, whilst crystals of silver nitrate under the same conditions remain, as in the other case, unaltered below a thin crust of silver oxide.

Now, as for every molecule of cupric sulphate a molecule of cupric sulphide is formed, whilst the water of crystallisation, having been solid before, passes into the liquid state, it follows that the crust of cupric sulphide must contain a great many more molecular gaps than that of silver sulphide, for this reason, that silver nitrate contains no water of crystallisation.

A crust of sulphide once formed, the process of decomposition will go on in the same manner as before, only when the molecular gaps are large enough to allow of the passage of more molecules of potassium sulphide, whilst when the gaps are too small we shall have chemosmotic decomposition, or electrocapillary phenomena. The potassium unites with the group SO_4, metallic copper being separated, whilst the sulphur previously combined with the potassium remains outside the endosmotic layer, forming potassium disulphide. The crust of silver sulphide, on the other hand, having no gaps, soon puts a more or less complete stop to the chemical action.

The author is of the opinion that many of those chemical processes which take place in animal and vegetable organisms may be explained in a similar manner by supposing that the cellular membranes are

* J. pr. Chem. [2], iv, 271.

provided with gaps, and possess a different molecular structure for each species of cells. The substance outside the membrane being prevented, in consequence of its molecular volume, from passing through, will, according to its chemical constitution, be split up into less complex molecules, which are better able to make their way into the interior. Thus the alcoholic and the lactous fermentation may be accounted for by the structure of the cells of those fungi, the presence of which is indispensable for the different kinds of fermentation. The decomposition of carbonic acid by the action of sunlight, as well as the peculiar function of the periosteum, which by a kind of filtering process withdraws from the blood the materials for the formation of bones, may both be chemosmotic processes.

R. S.

On Luminous Tubes with Exterior Electrodes. By ALVERGNIAT.*

THE author reviews various difficulties and irregularities attending the use of internal metallic electrodes, and points out that these may be avoided by placing the electrodes outside the tubes without much loss of brilliancy. He also states that when such external metallic electrodes are used with the induction coil, a large quantity of ozone is produced round the apparatus.

A. D.

On the Measurement of the Chemical Intensity of Total Daylight made at Catania during the Total Eclipse of December 22, 1870. By H. E. ROSCOE, F.R.S., and T. E. THORPE, F.R.S.E.†

THE method of measurement adopted is that described in the Bakerian Lecture for 1865. The observations were made in the garden of the Benedictine Convent of San Nicola, at Catania. In order to obtain data for determining the variation in chemical intensity caused by the alteration in the sun's altitude during the eclipse, observations were made on the three previous days. The results obtained confirm the conclusion formerly arrived at, "that the relation between total chemical intensity and sun's altitude is represented by a straight line."

During the greater part of the eclipse, observations were made every ten minutes, although for some time before and a short time after totality, it was impossible to make any observations, as the sun was never free from clouds for more than a few seconds at a time.

During totality the chemical intensity of the feebly diffused light was attempted to be estimated, the sun's disc and the greater part of the heavens being obscured by clouds at this time. The sensitive

* Compt. rend., lxxiii, 561. † Proc. Roy. Soc., xix, 511–514.

paper was exposed for ninety-five seconds, but not the slightest action could be detected. It is estimated that the chemically active light present was certainly not more than 0·003 of the unit adopted, probably much less.

From the observations made during the partial phases, the law seems established "*that the diminution in the total chemical intensity of the sun's disc during an eclipse is directly proportional to the magnitude of the obscuration.*"

The question of the variation of the direct and the diffused light is discussed in the original memoir. It was found that the rate of diminution in chemical action exerted by the diffused light is, up to a certain point, greater than corresponds to the portion of the sun eclipsed, whilst from this point up to totality the rate of diminution became less than corresponds to the progress of the eclipse. The same fact was noticed by Captain J. Herschel during the eclipse in 1868. It is due to the dark body of the moon cutting off the light from the brightly illuminated portion of sky lying round the solar disc.

A. P.

On the Reversal of the Lines in the Spectra of Metallic Vapours. By A. Cornu.*

The author had been engaged in photographing the triple band (between H and L) in the spectrum of the magnesium spark, to which, in great measure, the photogenic energy of the spark is due. He repeated the experiments with a more powerful apparatus, consisting of a large induction coil set in action by a battery of 18 Bunsen's cells, arranged in a series of 8 pairs, and a spherical condenser of 40 centimeters diameter; the electrodes were formed of pieces of magnesium, 10 mm. thick. On examining the photographic image produced by the spark from this apparatus, he found, to his surprise, five bands instead of the usual three, each of the two least refrangible bands being divided into two ill-defined bands. This experiment was repeated 25 times, with the same result. After satisfying himself that the effect was not due to faulty adjustments, the author concluded that this division of the bands is due to reversal He quotes an observation of P. Secchi, recording the reversal of only one, the least refrangible one, of the three lines of magnesium (*b*) in the spectrum of a sun-spot, as analogous to the observed reversal of two only of the three lines. The author did not succeed in reversing the *b* band of magnesium with the spark from a most powerful induction coil, but succeeded easily in so doing by the help of the electric arc from 50 elements.

To effect this the author recommends the following arrangement:

* Compt. rend., 1871, lxxiii, 332—337.

—A disc of carbon, 6 to 8 centimetres in diameter, forms the positive pole, and the fragment of metal is placed in a hollow on the surface of this disc; the negative carbon point is then brought down until the spark passes, when it is raised until an arc of 4 or 5 mm. is formed. By means of a lens the image of this arc is thrown on the slit of the spectroscope, when, in the case of magnesium, the triple line *b* appears clear and sharp. The carbon point is now gradually lowered, when the lines widen, become indistinct, and soon a very fine black line appears on the least refrangible of the lines. On bringing the carbon still lower, the second, and finally the third line are reversed. The author has tried several metals with similar results. As a rule, the reversal began with the least refrangible of a group of lines, extending to the others as the temperature was gradually raised.

The following list contains the groups of lines of various metals, reversed by the author. The metals are arranged nearly in the order of the case with which the reversal is effected. The wave lengths (λ) are given in millionths of a millimeter.

Sodium, line D		$\lambda = 589$
Thallium, green line		$\lambda = 535$
Lead, violet line		$\lambda = 406$
Silver	green line	$\lambda = 546$
	green line	$\lambda = 521$
	violet line	$\lambda = 424$
Aluminium, violet lines		$\lambda = 396$
	Between H_1 and H_2	$\lambda = 394$
Magnesium triple green line		$\lambda = 518{\cdot}30$ (the least refrangible)
Magnesium triple violet line		$\lambda = 383{\cdot}78$ (the least refrangible)
Cadmium	green line	$\lambda = 509$
	bluish green line	$\lambda = 480$
	blue line	$\lambda = 467{\cdot}7$
Zinc	green line	$\lambda = 481$
	green line	$\lambda = 472$
	blue line	$\lambda = 467{\cdot}8$
Copper, green line		$\lambda = 510$

Iron, cobalt, bismuth, antimony, and gold, did not present any appearance of reversal. Alkali-salts, especially the chlorides, exhibit the reversal of the bright lines still more easily. Sodium chloride $\gamma = 589$ and 422, and lithium chloride γ 670 and 458, are the most remarkable. The author briefly considers the relation of the above experiments to the spectroscopic observations of the sun; he maintains that these experiments establish two facts.

1st. That an extremely thin stratum of vapour is sufficient to produce

reversal of the lines, a stratum so thin as to be quite inappreciable at our distance from the sun being all that is necessary.

2nd. That it is unnecessary to imagine that a continuous atmosphere, however thin, exists round the sun, as the absorption is quite local, and is produced spontaneously by the cooling of the outer parts round each incandescent centre.

A. D.

On the Spectra of bodies belonging to the Nitrogen and Chlorine Groups. By A. Ditte.*

I. *Nitrogen Group.*—The author studied the spectra of phosphorus, arsenic, antimony, and tin, by passing the induction spark through the vapour of the chlorides of these bodies. He comes to the following general conclusions :—

1. The spectra expand more and more, especially towards the violet end, as we pass from nitrogen to tin, or in proportion as the properties of the element approach those of the metals.

2. The spectra of all have three maxima of luminous intensity due to very brilliant lines, separated by comparatively dark intervals.

3. As we pass from nitrogen to tin, the three maxima move towards the violet end of the spectrum.

II. *Chlorine group.*—The spectra of bromine and iodine were observed by passing the induction spark through the vapours of bromide of arsenic, or the chlorides of bromine or iodine, of course eliminating the spectra of arsenic or chlorine. The following are the conclusions arrived at :—

1. In passing from chlorine to iodine, the spectra expand gradually towards the ultra violet, though not in so marked a manner as in the other group ; at the red end the spectra seem rather to contract.

2. Each spectrum has two maxima of light.

3. These maxima approach each other as we pass from chlorine to iodine, and consequently the brilliant portion of the spectrum diminishes; the brilliant lines seem also to become broader.

4. The maxima move towards the violet end as we approach iodine.

III. The author has also examined the spectrum of fluorine produced by passing the induction-spark through silicon fluoride. The spectrum has two well defined maxima, but does not present the brilliant region peculiar to the spectrum of the chlorine group, and the maxima are wide apart. The author considers that, according to its spectrum, fluorine ought not to be placed among the halogens.

In conclusion, the author points out the general agreement of the characters of the spectra in the various groups, examined by MM. Troost

* Compt. rend., 1871, lxxiii, 738—742.

and Hautefeuille and himself, and draws attention to the fact that these spectroscopic observations confirm the order in which Dumas placed these bodies in his classification of the elements in natural families.

A. D.

On the Spectra of Sulphur, Selenium, and Tellurium. By G. Salet.*

The author states that various errors have crept into the spectroscopic analysis of the attenuated matter contained in Geisler's tubes. He quotes as an instance the supplementary spectra of hydrogen described by Wüllner. He, however, considers that the discovery of Plücker, at all events as far as sulphur is concerned, is not shaken by the facts brought forward by Ångström, and that sulphur has really two distinct spectra, one consisting of lines, the other of bands, the former produced by the disruptive discharge, the latter by less intense discharges, or when sulphur vapour is rendered incandescent in a hydrogen flame, and is shown, though less sharply, in the absorption spectrum of sulphur vapour. He gives measurements of the lines and bands obtained by the above methods, confirming the existence of two distinct sulphur spectra.

Selenium, like sulphur, gives two spectra, one consisting of bands, the other of lines; the author describes the former only. This spectrum he obtained either with electricity of feeble tension, or by volatilising selenium in a hydrogen or coal-gas flame. The wave-lengths, corresponding to the middle of the bands, are as follows (in millionths of a millimeter).

Selenium.

Electricity.	Combustion.
587	
579	
565	565
550	550
537	537
527	527
516	516
505	505
495	495
484	484
indistinct	475
to	467
440	indistinct
	to
	410

* Compt. rend., lxxiii, 559—561, and 742—744.

The luminous bands of selenium are nearly twice as far apart as those of sulphur, but, contrary to expectation, the bands of tellurium were not found to be separated by a wider interval.

The author passed the spark through tellurium vapour contained in a tube of Bohemian glass. He states that the most refrangible of the bands observed were, perhaps, due to tellurous acid. The spectrum was also observed by volatilising tellurium in a current of hydrogen, and burning the gas from a platinum jet.

The following are the measurements of the wave lengths (in millionths of a millimeter):—

Tellurium.

Electricity.	Combustion.	Electricity.	Combustion.
625	625	492	— Indistinct
615	615	487	— Indistinct
605	605	482	— Indistinct
594	594	477	476
Maximum 584	585	Strong 473	472
573	574	467	467
566	566	460	— Indistinct
556	556	456	— Indistinct
547	547	451	— Indistinct
542	542	447	447
534	534	Indistinct 440	440
Minimum 528	527	435	435
522	522	433	— Indistinct
516	515	428	— Indistinct
507	507	Approximately 425	— Indistinct
502	501	420	— Indistinct
498	496	415	— Indistinct

A. D.

On the Spectra of Sulphur, Selenium, and Tellurium. By A. Ditte.*

The author has examined the spectra of the above three elements by passing the spark from an induction coil through the vapours of their chlorides. Eliminating the lines which are alike in the three spectra, due to the chlorine, the rest lead to the following conclusions:—

The spectrum of sulphur extends between the divisions 22 and 120 of the micrometer. It shows two maxima, one being a double line in the yellow, the other, and brighter, a band at the commencement of the blue.

The spectrum of selenium begins at division 19 and ends at 125, and also shows two maxima consisting of double lines, the first between the yellow and green, the second in the blue.

* Compt. rend., lxxiii, 622.

The spectrum of tellurium begins at 18 and ends at 146, and, like the former, shows two maxima, one in the indigo, the other in the violet.

The spectra thus increase in range, more particularly towards the ultra-violet end, as we pass from sulphur to tellurium, or towards the body approaching the metals in its characters. Each of the spectra shows two maxima, one being superior to the other, and as we pass from sulphur to tellurium the two maxima move towards the violet end.

In conclusion, the author observes that his examination of these three spectra shows selenium to be intermediate between sulphur and tellurium, a conclusion confirmed by the other properties of these three elements.

A. D.

On the Spectra of Carbon, Boron, Silicon, Titanium, and Zirconium. By L. Troost and P. Hautefeuille.*

The authors examined the spectra of the above elements by passing the induction spark through atmospheres containing either fluoride of boron or of silicon, or the vapour of chloride of carbon, boron, silicon, titanium, or zirconium. The spectra were compared, after eliminating the lines due to chlorine or fluorine common to all. The following are the conclusions arrived at by the authors:—

As we pass from carbon to zirconium, or, in other words, from metalloïds to metals, the rays become more and more refrangible.

The spectrum of each element has three maxima, caused by groups of luminous bands.

As we pass from carbon to zirconium, the three maxima advance more and more towards the violet. Thus the least refrangible maximum in the spectrum of carbon is midway between D and E; in that of boron it corresponds with E; in the case of silicon it is between E and F; with titanium a little beyond F; and, finally, in the spectrum of zirconium it is between H and L. The most refrangible maximum is near G in the case of carbon, and far in the ultra violet in the case of zirconium.

Thus a consideration of the spectra of these elements confirms the order in which they have already been placed according to their other properties.

A. D.

On the Spectra of Tin and its Compounds. By G. Salet.†

A few substances require the employment of hydrogen and the cooling of a portion of the flame in order to give well-developed

* Compt. rend., lxxiii, 620—622. † Compt. rend., lxxiii, 862–3.

spectra on combustion. The author has already described the spectrum of sulphur obtained under these conditions, and intends to return to that of phosphorus, which, in addition to the rays indicated by Christophle and Beilstein, contains several interesting bands.

When a small quantity of stannic chloride is volatilised in a current of hydrogen, the flame is coloured blue, and gives off white fumes of stannic acid. Its core appears to consist of two concentric cylinders, of which the internal one is blue, and the other is coloured of a feeble carmine tint. The different portions of the flame may be analysed without modifying their disposition. It is only necessary to throw on the slit of the spectroscope the image of the flame produced by a lens of short focus; the spectrum is thus divided into several bands, each corresponding to one portion of the flame. The internal cylinder gives a continuous spectrum, the blue flame a primary spectrum, made indistinct by the combustion, and presenting the following bands:—

From 615	532;	From 450 } triple band
To 580 (max.);	From 520	To 439 }
566;	To 497 (max.);	From 433 } id.
563;	(With max. at 516 to 510);	To 424 }
556;	From 494	From 414 } feeble and
From 545	To 480 (max.);	To 408 } indistinct
To 537 (max.);	From 470 } feeble	
	To 460 }	

The carmine-tinted cylinder gives a single ray at 610, coincident with the second ray of lithium, Li β. The cooled portion of the flame yields a beautiful carmine coloration, exceedingly well adapted to spectroscopic examination. The red ray, under these circumstances, is well seen; its edges are faint. In this particular it differs from Li β, which, however, is not seen in this region of the flame, and would, moreover, be accompanied by Li α if the red colouration were due to lithium. It is also necessary to point out that lithium salts could scarcely be brought into the flame by the vapour emitted by stannic chloride at the ordinary temperature. The author has, in addition, obtained the new ray of tin from many of the volatile compounds of this body, and even from the metal itself. Lastly, Mr. Barrett has observed that the flame of hydrogen becomes tinged with red when brought into contact with tin. By using bromide of tin, or by bringing a drop of bromine in proximity to the flame, the core, originally blue, becomes coloured bright green, the flame itself continuing to be blue, and giving the spectrum above described. The green core gives a continuous spectrum; in the cooled flame the green colour appears in immediate contact with the cold body, and with a brilliancy which reminds one of phosphorus. At the edge of the green portion, and in

the hotter parts of the flame, the red coloration giving the single ray at 610 may be recognised. Iodide of tin gives similar results; the core is yellowish, and gives a continuous spectrum. It follows, therefore, from these experiments, that each of the volatile tin compounds gives three spectra when introduced into the hydrogen flame, two of which are common to all, the third being continuous. The first corresponds to a moderately high temperature, and to a reducing atmosphere; it is the spectrum of the metal, and is characterised by the narrow band at 610. The second is produced at a still higher temperature, and in the zone of combustion; it is doubtless due to tin oxide. Lastly, the third varies with the salt used; it is continuous, and corresponds to a temperature comparatively very low.

T. E. T.

On the Calcium Spectrum. By R. Blochmann.*

Pure calcium chloride was obtained by leaving a solution of the salt in contact with a solution of calcium sulphate, to remove every trace of strontium, and then subjected to an eleven times repeated fractional precipitation with oxalate of ammonium. The pure salt finally obtained, on being introduced into the flame of the Bunsen burner, furnished in the first moment a very bright spectrum, which, however, quickly disappeared, and was after a little time succeeded by another, less bright but of longer duration. By the evaporation of the water generally present in the calcium chloride, some particles of calcium are mechanically carried away and dispersed through the flame: hence the instantaneous spectrum. The calcium chloride being melted, evaporates, and produces the second feebler spectrum, until it is converted either in an allotropic modification or a basic salt, which, being not volatile, furnishes no spectrum at all. By using the hydrogen flame a very much brighter spectrum was obtained; less time elapsed before the appearance of the second, and especially the blue line, only rarely and indistinctly to be seen in the flame of the Bunsen burner, was always very distinct. The orange-red band had gained in breadth, and showed three different tints, blood-red, fiery-red, orange-red, rendering it probable that the red band is produced by three lines of different tints. As the strontium lines were still visible, it appears that contact with sulphate of calcium does not remove the whole of the strontium from a solution of chloride of calcium.

The complete spectrum consisted of—

* J. pr. Chem. [2], iv, 283.

A crimson band.....	from	5·3	to	5·5
Three red bands.....	,,	5·7	,,	6·1
One orange-red band....	,,	6·25	,,	6·45
One orange-yellow line..	,,	6·60		
The sodium line.....	,,	6·60	,,	6·75
One yellow-green line ..	,,	6·9	,,	7·0
One green line	,,	7·15	,,	7·25
One green band.....	,,	7·6	,,	7·9
One green line	,,	7·2	,,	8·6
One violet line	,,	15·0	,,	15·1

Just before the disappearance of the first bright spectrum some green and blue lines were seen between 8 and 15, which, if they are not exclusively due to a very high temperature, seem to point out the presence of a new element.

R. S.

On the Theory of the Colours of Natural Objects. By W. STEIN.*

THE author finds that a mixture of $4\frac{1}{2}$ parts ultramarine, 6 pts. uranium oxide, and 1 pt. red lead, which is of a dirty violet colour when dry, appears black when made into a paste with water or alcohol; and when the paste is stirred up with the white powder of barium sulphate or carbonate, the mixture appears blue. The author does not seem to be acquainted with recent investigations connected with the subject of his paper.

R. S.

On the Clean Surface possessed by Films of Albumin and Tannin, and their use in Photography. By CARL SCHULTZ-SELLACK.†

ON a glass surface, which has been exposed to the air for some time, steam is condensed in drops, but if the perfectly clean surface is completely moistened with water, the film, on drying, becomes uniformly thinner, so as to show Newton's colours. When it is once dry, however, the steam again condenses in drops. On the other hand, films of albumin, tannin, and other vegetable extracts behave like perfectly clean surfaces, even after drying, and hence their use in photography. The dry collodion plate is covered with a film of these substances and thus preserves a perfectly clean surface even after drying. Besides this, these substances may also act beneficially by their hygroscopic character.

A. D.

* J. pr. Chem. [2], iv, 276. † Pogg. Ann., cxliv, 171.

Inorganic Chemistry.

Researches on the intimate Action of Substances which assist the Decomposition of Potassium Chlorate and the Disengagement of Oxygen. By ERNEST BAUDRIMONT.*

IN the *Comptes rendus* for 1855 (t. xli, p. 341), MM. Thenard gave the results of numerous experiments upon the principal chlorates, bromates, iodates, &c., when heated with various substances, and they state that the different mixtures evolve gas at 100° below the temperature at which the gas is disengaged when the chlorates, &c., are heated alone. In the "Journal de Pharmacie" for 1856, Buignet gives an analysis of certain notes and memoirs published in the "Pharmaceutical Journal" by Messrs. Hornsby, Witt, and Brown; and in the same French journal (t. xxix, p. 365) is a memoir by Schönbein.

Hornsby has pointed out that oxygen gas disengaged from chlorate of potash in presence of binoxide of manganese, is always accompanied by chlorine, with production of a brilliant and intermittent light, which he attributes to electricity, engendered by the molecular change of the gaseous particles. On the other hand, Witt maintains that the oxygen obtained from such a mixture at a high temperature possesses much more combustible energy than the same gas prepared at a low temperature; and that the sparks observed by Hornsby are due to organic matters which, by chance, were in contact with the gas. Witt also recalls the two phases of the decomposition of potassium chlorate originally observed by Sérullas, and confirmed by Millon.

1st phase.... $2(KClO_3) = KClO_4 + KCl + O_2$.
2nd ,, ... $KClO_4 = KCl + O_4$.

The oxygen produced in the second stage of the reaction is much more active than that produced in the first stage: as, like ozone, it turns iodised test-paper blue. The same character is also met with in the oxygen prepared from potassium chlorate by the aid of manganese dioxide, although the latter merely facilitates the evolution of oxygen.

Brown impugns this theory, and shows that one-tenth only of manganese dioxide is sufficient for the decomposition of the potassium chlorate, and further states that the enormous heat produced is much greater than that derived from the source employed, the mass becoming partially incandescent; also that the manganese dioxide acts by its proper nature, as it is not capable of being used a second time. He attributes the pretended activity of the gas obtained under these circumstances to

* J. pr Chem. [4], xiv, 81—94; and 161—177.

the presence of chlorine disengaged in the decomposition operation, an opinion which Witt combats by new experiments.

Schönbein suggests that potassium chlorate is a combination of potassium chloride and ozone, and that heat converts ozone into ordinary oxygen, which cannot then remain united to the potassium chloride.

Deville compares the decomposition of potassium chlorate by heat to the ebullition of water charged with a salt, the solution becoming concentrated as the vapour escapes. Here the vapour is oxygen and the potassium chloride produced becomes the salt which is concentrated. On adding a foreign body, oxide of copper, oxide of manganese, &c., to the chlorate in fusion, these auxiliaries of ebullition evidently favour the disengagement of oxygen as they would favour in water the production of vapour. This theory is, however, refuted by the fact that potassium chlorate loses its oxygen without entering into fusion.

Berthelot, in his *Researches upon Thermo-chemistry* (*Ann. Ch. Phys.* 865 [4], vi, 290), classes chloric acid amongst *endothermic* bodies. In this view he is supported by Frankland, who states that in the combustion of organic matters by potassium chlorate, more heat is evolved than when free oxygen is used.

Action of Heat upon Potassium Chlorate.—The melting point of potassium chlorate, as determined by Berthelot's air-thermometer, is about 370°, and soon after its change of state the points nearest the light begin to emit gaseous bubbles, but the evolution of gas is not much manifest until towards 400°. 100 grams of potassium chlorate were melted and made to lose by heat 8·5 grams of oxygen; the mass which remained was found to contain 56·7 potassium perchlorate, 27·2 potassium chloride, and 7·6 undecomposed chlorate.

50 grams of the salt strongly heated in a platinum crucible partly covered with another crucible of the same metal, became considerably inflated after complete fusion and partial decomposition; a hissing noise was heard, and the slightly red mass became fully incandescent; then in an instant the ignition ceased, the salt solidified entirely, and all evolution of gas ceased. The phenomenon of incandescence cannot be attributed to the heat emitted by the fire, and therefore potassium chlorate must be regarded as an *endothermic* body.

Decomposition of Potassium Chlorate under the influence of bodies which do not act Chemically upon it.—To study this phenomenon methodically, a large test tube was fitted with a cork having three holes; one received a thermometer going up to 360°; another carried a tube bent at right angles, and descending to the bottom of the test-tube, to carry there a current of pure carbonic acid gas; and the third was furnished with another bent tube, having several branches destined to conduct the gas into graduated vessels

placed over mercury. The test-tube was plunged into a flask three-fourths filled with mercury, and resting on a sand-bath heated by a gas-light. By these arrangements it was easy: 1st, to gradually raise the mercury in the flask to ebullition, so as to have a constant temperature; 2nd, to expel the air from the apparatus by a current of carbonic acid gas; 3rd, to collect the oxygen evolved; 4th, to determine the temperature at which the decomposition commenced; 5th, to compare the course of the thermometer with the rapidity of the evolution of oxygen; 6th, to ascertain the loss of weight by the mixture; and 7th, to estimate the amount of potassium chloride formed.

In the test-tube was placed an intimate mixture of 4 grams of pure and finely pulverised potassium chlorate, with 1 gram of black copper oxide, obtained in the moist way; the air was then expelled by a current of carbonic acid. The mercury into which the test-tube was plunged was then heated, and the thermometer observed. At about 240° bubbles of gas, insoluble in caustic potash, showed themselves distinctly, and the evolution of gas continued slowly and regularly between 240° and 250°; it became more and more rapid in proportion as the temperature rose, especially between 295° and 300°; past this point, it was almost violent, and at about 305° or 310° *the mercury of the thermometer suddenly rose to over* 360°, whilst that of the flask was still far from its boiling point; the oxygen of the chlorate was evolved as at a single explosion, carrying with it some of the chlorine; then the disengagement of gas entirely ceased, and the thermometer fell rapidly to 310° or 305°. The operation was then suspended. There was no manifestation of incandescence.

After perfect cooling, the loss in weight of the test tube was found to be 1·60 grams. 4 grams of potassium ought to yield 1·56 grams oxygen; the salt was therefore entirely decomposed. The excess of loss of 0·04 gram must be attributed to the chlorine evolved with the oxygen, and to traces of water expelled from the apparatus. This was verified by estimating the amount of potassium chloride remaining in the tube by a standard solution of silver nitrate, the amount indicated being 2·40 grams, instead of 2·44 grams, as required by calculation. The weight of copper oxide had undergone no change.

The above results show that in presence of copper oxide—1st. Potassium chlorate can give up its oxygen at 150° or 160° below its normal temperature of decomposition. 2nd. The disengagement of gas takes place with great rapidity, and with extreme facility. 3rd. At a given moment it does so with emission of heat, due solely to the decomposition of the salt itself. 4th. It loses all its oxygen, together with a little chlorine, and is totally converted into decomposed potassium chloride. 5th. The copper oxide is not modified in any way.

The decomposition of potassium chlorate being accompanied by an

evident disengagement of heat, the salt is truly an *endothermic* compound, and it was desirable to know how far the temperature extended beyond that which could be indicated by the mercurial thermometer. For this purpose Berthelot's air thermometer was used; and on repeating the experiment as before, the disengagement of gas was found to follow the same course, escaping in torrents at 300°, when the temperature rose all at once to 390°, without any sign of ignition. The experiment was repeated with substitution of manganese dioxide for the black copper oxide, and the temperature rose suddenly from 300° to 396°.

If, instead of heating the mixture in a mercury bath, it be carried to a higher temperature, the incandescence of the mass is readily produced. A thin platinum crucible was heated on a sand-bath to a temperature nearly approaching dull redness. The mixture of potassium chlorate and copper oxide was then introduced; it fused, boiled quietly, then more quickly, afterwards swelled up, and soon afterwards the decomposition was terminated by a general incandescence, leaving the crucible below a dull red heat.

Influence of the nature of the body in contact.—The following results are from experiments made upon 4 grams of chlorate of potash, and 1 gram of the substance added. *Spongy Platinum.*—No action whatever up to 360°. When the two substances are fused together, the evolution of oxygen may be a little accelerated, but there is no incandescence. This result does not agree with Deville's theory. *Mercuric Oxide.*—No action whatever up to 360°, the oxide being found intact after the operation. *Silver Oxide.*—Gas is evolved at 220°, due, however, to the decomposition of the oxide. This soon ceases, and there is no further reaction even at 360°. Heated more strongly, the chlorate quietly decomposes with formation of silver chloride and caustic potash. This result is opposed to the opinions of Schönbein and Witt, who say that the action of this oxide upon the chlorate is very energetic. *Potassium Permanganate.*—Gas is slowly evolved at 360°, and the decomposition of the two salts proceeds simultaneously. Permanganate of potash decomposes at about 250° into oxygen, potash, and manganese sesquioxide; the last-named then reacts upon the chlorate, and transforms it little by little into potassium chloride and oxygen, and the temperature does not rise beyond 360°. *Black Oxide of Copper.*—Result already given (p. 1153). *Native Manganese Dioxide.*—Sensible action, even before 200°, becoming continuous about 250°, and even violent about 310°—320°, the thermometer rising beyond 360°. The loss in weight is 1·62 grams, the excess over the calculated loss, 1·56 grams, being due to the evolution of a little chlorine. *Ferric Oxide.*—Action begins about 250°, but is not continuous until 320°—325°. The evolution takes place readily, but there is no sudden elevation of tem-

perature, and the total decomposition of the salt requires a long time. *Black Oxide of Cobalt, Brown Oxide of Manganese, Dioxide of Lead.*—Action more feeble than with the substance previously named. A long time is necessary for the evolution of all the oxygen, and the temperature does not pass beyond 360°. The composition of these bodies undergoes no change during the reaction. All the preceding mixtures undergo true fusion when the temperature rises to 360°. The more feeble the action of the oxide, the less is the amount of chlorine evolved with the oxygen. *Alumina.*—Whether this body acts chemically or by contact only, the author is not prepared to say. Gas is evolved from 250°, but so much contaminated with chlorine, that the alumina appears to act as an acid. After the reaction the residue is alkaline, and the amount of potassium chloride present is 2·19 grams, instead of 2·44 grams, as required by theory.

Influence of the State of Division of the Substances.—Potassium chlorate is decomposed in presence of cupric oxide, with much greater facility when the salt is finely sifted than when only coarsely pulverised. 5 grams of a mixture of coarsely pulverised chlorate, with one-tenth of its weight of cupric oxide, lost only 0·60 gram of oxygen, at 360°, whilst in a similar experiment with the salt finely sifted, the loss was 1·88 grams. But the influence of the state of the bodies is more plainly seen by comparing the effect of black copper oxide, obtained in the moist way, with that obtained by ignition. The former decomposes the salt with great facility, and produces incandescence of the mixture when present to the extent of one two-hundredth part; while the latter acts only towards 310°—320°, causing a very slow and feeble evolution of gas, and scarcely producing incandescence when present as a twentieth part. So also manganese dioxide and ferric oxide, obtained in the moist way, act with much more facility than native manganese dioxide and ferric oxide obtained by ignition.

Influence of the Proportion of the Active Substances as compared with the Amount of Potassium Chlorate.—The active substances used were black copper oxide, manganese dioxide, and ferric oxide, in proportions varying from one-half to one five-hundredth part of the mixture. The author gives several tables which show the percentage weight of oxygen obtained from each mixture, and the progressive course of the decomposition both up to 360°, and at a dull red heat. The results may be thus briefly summarised. Although it is surprising how much the decomposition of the chlorate is accelerated by even so small a proportion of the active substance as one five-hundredth part, yet the greater the proportion of the latter the more rapid is the decomposition, and the greater is the proportion of the chlorate decomposed; but there is no relation between these proportions

and the equivalents of the substances employed. The mixtures in equal parts do not undergo any fusion at the temperature of boiling mercury, and only imperfectly when heated on a sand-bath. The phenomenon of incandescence is never produced when the maximum temperature is 360°, but is developed with great facility (the mixture in equal parts excepted), when a dull red heat is attained.

Influence of Temperature.—The decomposition of the mixtures generally commences at about 240°, or towards 300°, when the active substance is present in very small proportion. Even at these low temperatures the mixture can be completely decomposed, but the evolution of oxygen is very slow, and the mixture does not enter into fusion. Oxygen so prepared is perfectly free from chlorine. When the temperature is raised to 310°—320°, gas is evolved violently, there is an emission of caloric, without ignition, and the temperature passes all at once beyond 360°, at the same time chlorine is liberated, and the mass undergoes complete liquefaction. At a still higher temperature the evolution of gas is still more rapid, and, in fact, the rapidity of the decomposition is in porportion to the temperature.

Chemical Actions which certain Substances Exercise upon Chlorate of Potash.—Potassium chlorate causes the inflammation of sulphur, wood-charcoal, graphite, sulphide of antimony, &c., below the temperature of boiling mercury, and during the reaction there is an enormous development of heat. Substances which react upon this salt generally take from it its oxygen, rarely its chlorine, and sometimes also seize its potash; when the last named reaction occurs there is always a large quantity of chlorine produced, due to the decomposition of the chloric acid liberated. When green oxide of chromium is heated in a mercury-bath with this salt, a considerable evolution of chlorine and oxygen occurs even below 200°, and the oxide is completely transformed into potassium chromate below 290°. Metastannic acid has no action upon the chlorate at 360°, but at a higher temperature chlorine and oxygen are evolved, and the residue is strongly alkaline. Tungstic acid begins to act upon the salt at 270°, and at 350° there is evolution of oxygen with much chlorine, and the probable formation of an alkaline tungstate. Silicic acid acts only beyond the melting point of the chlorate, with evolution of oxygen, chlorine, and excessively pungent white vapours, which may be chloride of silicium. Fused boric acid acts energetically, chlorine being liberated in great abundance. J. B.

On the Calcination of Lead Oxalate. By E. Maumené.*

The black product left on calcining lead oxalate was considered by Berzelius, and after him by Dulong, to be a suboxide of lead. Sub-

* Mémoire sur la Calcination de l'Oxalate de Plomb. Paris, 1871.

sequently, Boussingault found that on exposing this body in a muffle to an incipient red heat, it experienced a gain in weight corresponding to the difference between Pb_2O and $2PbO$. Lastly, its formation and properties were examined by Pelouze, who found, on keeping the oxalate at a temperature of 310°, at which it begins to decompose, that the gases disengaged are carbonic oxide and carbonic acid, in the ratio of $1CO : 3CO_2$, according to the equation, $2C_2O_4Pb = Pb_2O + CO + 3CO_2$.

Maumené, however, finds: 1. That the black residue is a mixture of metallic lead with the monoxide PbO, inasmuch as, when triturated with mercury for a considerable time—or for a shorter time if previously moistened with alcohol—it yields an amalgam of lead, and when boiled with a solution of sugar, it gives up a considerable quantity of lead oxide.

2. That the proportions of carbonic oxide and carbonic acid evolved in the decomposition are not constant, but vary according to the temperature and other conditions of the experiment. When the oxalate was heated in an oil-bath to 310 —315°, the gas collected in the early stages of the decomposition exhibited nearly the ratio $1CO ; 2CO_2$; but on collecting successive portions of the gas evolved at 315°, the proportion of carbonic acid was found gradually to increase, till at length the evolved gas consisted almost wholly of carbonic acid. This result is due to the gradual oxidation of the carbonic oxide by the lead oxide in the residue. Similar results were obtained at higher temperatures. By calcining a small quantity of the oxalate (1 gram) in a narrow gas tube, of which it occupied a considerable length, and using a regulated flame, the author obtained a gaseous mixture exhibiting very nearly the ratio $1CO : 3CO_2$, mentioned by Pelouze.

Researches upon the Reciprocal Transformation of the Two Allotropic States of Phosphorus. By G. Lemoine.*

The mutual transformation of the two allotropic states of phosphorus is distinguished by the extreme simplicity of its theoretic conditions. Ordinary phosphorus, heated above 260 in a closed vessel, is changed into red phosphorus, and the reverse takes place in starting with red phosphorus.

All the determinations were made at 440°, the temperature of boiling sulphur. Flasks containing a certain weight of phosphorus were heated to 200°, to drive off moisture, then securely closed, afterwards heated for some hours to 440°, and cooled quickly to avoid the influence of intermediate temperatures. The two allotropic modifications of phosphorus were then separated by carbon bisulphide.

* Compt. rend., 797—801; and 837—841.

Transformation of Red Phosphorus.—Various quantities of red phosphorus were heated for eight hours to 440° in flasks varying from 60 c.c. to 600 c.c., and the results showed that if the quantity of red phosphorus introduced be in proportion to the volume of the flask, the quantity of ordinary phosphorus obtained is itself proportionate to that volume. To quote two examples—red phosphorus, in the proportion of 16·05 grams and 16·02 grams per litre, was introduced into flasks of 516·8 c.c. and 91 c.c. respectively, and the amount of ordinary phosphorus obtained was at the rate of 4·55 grams and 4·65 grams.

The conversion is never complete, but approaches more nearly to completion the smaller the quantity of phosphorus operated upon. The limit is, in fact, determined by the tension of the vapour, as in the case of volatilisation and dissociation. In experiments upon 0·63, 1·81, 4·93, 16·05, 30·24, and 95·85 grams respectively per litre, the amounts of ordinary phosphorus obtained were 0·60, 1·33, 2·87, 4·55, 4·39, and 4·11 grams.

The quantity of ordinary phosphorus thus produced does not increase indefinitely with the amount of red phosphorus introduced, the best results being obtained at the rate of 16 grams per litre. In using large quantities, there is a partial change into red phosphorus of the ordinary phosphorus at first produced, and the two kinds become cemented together into lumps difficult to disintegrate.

The residue of red phosphorus separated by bisulphide of carbon, and heated anew, gives results similar to those mentioned, even after two successive operations, thus showing that it is chemically homogeneous.

In heating the phosphorus less than eight hours, the transformation is in general less complete. In small quantities heated beyond eight hours it is more complete; not so, however, with large quantities, owing to the before-mentioned tendency to agglomerate into lumps.

Transformation of Red Phosphorus under Pressure.—Similar experiments made in flasks containing nitrogen (the pressure at 440° being $1\frac{1}{2}$ atmos.), gave results differing but little from those stated, the quantity of ordinary phosphorus produced in each case being a little less.

Transformation of Ordinary Phosphorus.—The conversion of ordinary into red phosphorus becomes more and more rapid as the temperature is raised *in vacuo*, from 290° towards 440°, its boiling point. The rapidity of the transformation varies with the amount of phosphorus used, and diminishes as the limit is approached. At any given moment the rapidity depends not only upon the quantity of ordinary phosphorus remaining, but also upon

the quantity of red phosphorus already formed. The phenomenon is pre-eminently one of vapour tension, for in experiments with flasks of various sizes, if the quantity of ordinary phosphorus introduced be proportionate to the volume of the flask, the amount of ordinary phosphorus remaining at the conclusion of the experiment will also be proportionate to that volume. The transformation is never complete. With 30 grams per litre the amount of ordinary phosphorus remaining at the end of two hours is 5·3 grams; at eight hours, 4 grams; at 24 hours, 3·6 grams, which is the limit of the transformation, and this limit is also found when other quantities are used. There is thus a close identity in the amount of ordinary phosphorus remaining, whichever of the two allotropic states be used.

In a third paper (Compt. rend. lxxiii, 990—995) the author gives a mathematical exposition of the conditions of these transformations, in connection with a general theory of simple reactions limited by inverse action. J. B.

The Action of Ammonia on Phosphorus. By A. COMMAILLE.*

IN a previous communication the author has shown that when ammonia acts upon phosphorus a yellow substance is produced, and, further, that this substance differs from Thénard's solid phosphide of hydrogen, its composition being represented by the formula P_3H.

When the action of ammonia upon phosphorus is greatly prolonged the yellow compound first produced gradually deepens in colour, until it becomes almost black. At this stage the action of ammonia appears to be arrested, at least no further change in the appearance and physical properties of the phosphorus are produced by continuing the reaction, neither by treating it with supersaturated ammonia, nor by liquid ammonia aided by the application of heat.

Dry ammonia gas is altogether without action upon ordinary phosphorus; it is possible even to distil the phosphorus in an atmosphere of the gas without in any way affecting its external appearance, but if the gas be moist the phosphorus is slightly blackened. This result is contrary to that which is given in some works on chemistry. Solution of ammonium carbonate is likewise without action upon phosphorus.

When an alcoholic solution of ammonia is employed, the phosphorus gradually assumes a brown colour, while the liquid becomes turbid, and deposits small colourless crystals of phosphite and hypophosphite of ammonia. After a time a green powder, which disengages non-spontaneously inflammable hydrogen, separates from the unaltered phosphorus. If the liquid be heated the same ultimate result is obtained,

* J. Pharm. Chem. [4], xiv, 184—188.

with this peculiarity, that the melted phosphorus remains in the liquid state, and does not solidify even after many weeks. This circumstance has been previously noticed by Poggiale, in a communication upon the action of alcoholic potash upon phosphorus.

Although Flückiger has stated that the compound resulting from the action of ammonia aided by heat is an ammoniacal phosphide, the author finds that when the above-mentioned green substance is washed with warm water, until it returns to its original yellow colour, the wash waters are entirely without action upon red litmus paper, and do not consume a tenth of a cubic centimetre of standard acid; neither is it possible to detect an appreciable quantity of ammonia, when the phosphorus is heated to its decomposing point, and a current of hydrogen gas passed over it. The green phosphide behaves in a similar manner to Thénard's phosphide when treated with alcoholic soda solution; it produces a deep blood-red coloration, but while Thénard's phosphide is unaffected when boiled with concentrated hydrochloric acid, the former becomes suddenly of a dark ochreous tint.

Thénard's yellow phosphide, prepared by the action of hydrochloric acid upon the spontaneously inflammable gas, neither blackens, nor becomes green when treated with ammonia, but slowly dissolves. The compound P_3H, which blackens under the influence of ammonia, does not dissolve. In order to make certain that the latter compound did not contain any oxide of phosphorus, it was distilled in a current of hydrogen; a residue, consisting of an imponderable trace only of phosphorus acid, was obtained.

J. W.

On a New Phosphorus Oxychloride. By GEUTHER and MICHAELIS.*

UP to the present time, only one of the three phosphorus oxychlorides corresponding to the three phosphoric acids has been prepared, viz., $POCl_3$, corresponding to ordinary phosphoric acid. The authors have now succeeded in obtaining $P_2O_3Cl_4$, corresponding to pyrophosphoric acid. To denote this relation, the name *pyrophosphoryl chloride*† might be given to this body. It is produced by the action of nitrogen tetroxide upon phosphorus trichloride.

The best method of preparing it is to allow the vapours of liquefied nitrogen tetroxide (prepared by heating lead nitrate) to pass into the phosphorus trichloride cooled by a freezing mixture. The proportions are 20 grams nitrogen tetroxide and 100 grams of the phosphorus chloride. The reaction commences immediately, and nitrogen, nitric

* Deut. chem. Ges. Ber., iv, 766—768.

† The authors term the body "Pyrophosphorsäure chlorid."

oxide, and the vapours of nitrosyl monochloride (NOCl) are evolved. The phosphorus trichloride becomes reddened by the presence of the last-mentioned compound, and phosphorus pentoxide separates out. When the whole of the nitrogen tetroxide has been added, the freezing mixture is replaced by luke-warm water in order to distil off the nitrosyl chloride. The liquid remaining is then rectified. Much unattached phosphorus trichloride at first passes over, next a considerable amount of phosphoryl trichloride, after which the boiling point rises rapidly to 200°, between which temperature and 230°, the new compound distils over. It is advisable to prepare a large quantity of material by repetitions of the above operation before commencing to rectify. From 350 grams of phosphorus trichloride, the authors obtained 232 grams of phosphoryl trichloride, and only 40 grams (11·4 per cent.) of the new body.

This compound can also be prepared by the action of nitrogen trioxide on the phosphorus trichloride; in this way from 200 grams PCl_3 20 grams (10 per cent.) of the pyrophosphoryl chloride were obtained. The reaction was attended with the production of less $POCl_3$ and more P_2O_5 than in the preceding method. By rectification, the new body is found to boil between 210°—215°. It is a colourless liquid which decomposes slightly on distillation into phosphoryl trichloride and phosphorus pentoxide: $3P_2O_3Cl_4 = 4POCl_3 + P_2O_5$. It fumes in the air and carbonises corks. Its specific gravity is 1·58 at 7°. It does not solidify at − 18° on contact with a solid body. It is immediately decomposed by water, producing hydrochloric and ordinary phosphoric acids. The rational formula of the new body may be written—

$$\begin{array}{c} O \\ P^{v}O \\ Cl_2 \end{array}\!\!-\!\!-\!\!-\!\!P^{v}\begin{array}{c} O \\ Cl_2 \end{array} \quad \text{or} \quad P^{v}OCl_2\!-\!\!-\!\!-\!\!O\!-\!\!-\!\!-\!\!P^{v}OCl_2.$$

the two univalent groups, $POCl_2$, being held together by an atom of bivalent oxygen. This view of its constitution is confirmed by its reactions with phosphorus pentabromide or chloride and alcohol. In the first case, ordinary phosphoryl trichloride is produced: $P_2O_3Cl_4 + PCl_5 = 3POCl_3$; with PBr_5 we have $P_2O_3Cl_4 + PBr_5 = 2POBrCl_2 + POBr_3$. With alcohol ethyl phosphoric chloride is produced, of which a portion is decomposed by the water simultaneously formed, into ethylphosphoric acid and hydrochloric acid:

$$(1)\ 2P_2O_3Cl_4 + 4C_2H_6O = 4(PO.OC_2H_3.Cl_2) + 2H_2O$$
$$(2)\ PO.OC_2H_5.Cl_2 + 2H_2O = PO.OC_2H_5(OH)_2 + 2HCl.$$

The authors were unable to prepare the corresponding bromine compound. When nitrogen tetroxide reacts upon phosphorus tri-

bromide, phosphoryl tribromide and phosphorus pentoxide are alone produced.

T. E. T.

On the Solidification of Phosphoryl Trichloride and Phosphoryl Bromodichloride. By GEUTHER and MICHAELIS.*

IN attempting to prepare the preceding compound by mixing together phosphorus pentoxide and phosphorus pentachloride, according to the equation $3P_2O_5 + 4PCl_5 = 5P_2O_3Cl_4$, and exposing the mixture to a low temperature, the authors found that phosphoryl trichloride was alone produced. By still further cooling the liquid product, large colourless thin crystals were formed, consisting of solidified phosphoryl trichloride. When pure phosphoryl trichloride is cooled down to $-10°$ it remains liquid, even when shaken, but in contact with a solid body, such as the end of a glass rod, it immediately solidifies to a crystalline mass. The long colourless leaf-like or needle-shaped crystals melt at $-1·5°$. Below this temperature, they are permanent, and will lie upon ice for some time without being decomposed, and even when thrown into the cooled salt solution of the freezing mixture, they disappear only after a considerable time.

Phosphoryl bromodichloride may be also made to solidify in the same way. The large colourless crystals melt at $+11°$. The crystals of this compound appear to be isomorphous with those of phosphoryl trichloride and phosphoryl tribromide.

T. E. T.

Note.—The abstractor can confirm the above statement. It would appear, however, from his observations that the melting-point of $POCl_3$ is $+2·5$, and therefore is somewhat higher than that found by the authors. Phosphorus sulphochloride and vanadyl trichloride do not solidify under the same conditions as the phosphoryl compound.

T. E. T.

On Phosphorus Sulphobromide. By A. MICHAELIS.†

THIS compound was first prepared by Baudrimont,‡ who describes it as a yellow thick mass of disgusting odour. According to the author, however, it is one of the most beautiful of the compounds of phosphorus. It forms yellow octahedrons, which are easily obtained well developed from their solution in phosphorus bromide. It has a penetrating aromatic smell, melts at 35°, and its vapour attacks the eyes powerfully.

* Deut. Chem. Ges. Ber., iv, 769. † Deut. Chem. Ges. Ber., iv, 777.
‡ Compt. rend., [1], iii, 517.

When once melted it remains liquid for days, but solidifies immediately on contact with a solid body. On distillation it is decomposed into products which the author intends to describe in a future communication. It is easily soluble in ether, carbon disulphide, and the bromide and chloride of phosphorus. It decomposes very slowly in contact with water even when boiling: the products are sulphuretted hydrogen, sulphur, phosphoric and phosphorous acids. It is decomposed also but slowly by ammonia. With phosphorus pentachloride it yields phosphorus sulphochloride and phosphorus pentabromide, thus:

$$5PBr_3S + 3PCl_5 = 5PCl_3S + 3PBr_5.$$

In making this compound according to Baudrimont's method, viz., by the action of sulphuretted hydrogen on phosphorus pentabromide, it is necessary to treat the product with water to remove excess of the pentabromide, then to dry the mass between blotting-paper and dissolve it in carbon disulphide. The solution is next dehydrated by calcium chloride, decanted, and the carbon disulphide allowed to evaporate, when the sulphobromide crystallises out. In a future communication the author intends to treat of the action of sulphuric acid and of absolute alcohol upon this compound.

T. E. T.

Note by the Abstractor.—This compound could doubtless be more easily obtained by heating together phosphorus pentasulphide and pentabromide in the proportion indicated by the equation $3PBr_5 + P_2S_5 = 5PSBr_3$. T. E. T.

On the Existence of Sulphur Dichloride. By JOHN DALZELL and T. E. THORPE.*

WHEN dry chlorine in excess is passed through molten sulphur, a dark red fuming liquid distils over. This on renewed distillation begins to boil at 50° or 60°, and the thermometer slowly rises to 136°, at which point it remains stationary, and the orange-yellow disulphide Cl_2S_2 passes over. The fraction boiling below 136° frequently amounts to three-fourths of the original quantity of liquid; on again submitting it to distillation, the same order of things is repeated, and only a comparatively small portion distils over at 136°. At each distillation the liquid becomes light in colour, until at length, by long continued boiling it assumes the bright yellow of the disulphide, and boils constantly at 136°—137°. This behaviour would seem to indicate the existence of some compound of chlorine and sulphur which slowly undergoes decomposition on distillation, ultimately forming the disulphide, and the observations of Dumas and Soubeiran and of Marchand, Davy,

* Phil. Mag., Oct., 1871, 309.

and Rose, point to a body richer in chlorine. The disulphide and their analyses lead to the formula SCl_2. According to Carius, however, the amount of chlorine contained in the liquid over and above that required by the formula S_2Cl_2 is altogether dependent on the temperature. Hübner and Gueront have lately made an observation which tends also to support the idea of the existence of this body.* A quantity of the pure chloride S_2Cl_2 was placed in a strong freezing mixture, and a current of dry chlorine passed through it for some time, the excess of this gas (that is, that existing merely in solution) being displaced by a stream of dry carbon dioxide passed through it for three or four hours. The resultant product was then analysed, when numbers were obtained exactly agreeing with those required by the formula Cl_2S. The authors have repeated this experiment in a similar manner and with precisely the same results. They found that the product after chlorination contained (1) 69·25, (2) 69·06 per cent. chlorine; the formula SCl_2 requiring 68·93 per cent. It appears, therefore, to be proved that two compounds of sulphur and chlorine exist analogous to the oxide of hydrogen: it will, however, be remarked that whereas the most stable oxide of hydrogen is water, into which the dioxide is easily converted on heating, the reverse of this happens with the sulphur chlorides, the most stable compound being the S_2Cl_2, into which body and free chlorine, the compound SCl_2 is resolved on heating.

T. E. T.

On Iodosulphuric Acid and Iodosulphates, By SILVESTRO ZINNO.†

THE author obtained iodosulphuric acid, $SO_3I_2H_2$, accidentally, whilst endeavouring to prepare hydrobromic and hydriodic acids by the action of sulphurous acid upon bromide and iodide of starch. He compared its reactions with those of the acid prepared according to Pelouze and Frémy's method, by distilling a perfectly dry mixture of iodine and plumbic sulphite and rectification of the distillate over mercury, and found that the two acids were identical. He next tried to prepare iodosulphates by substituting a sulphite for the sulphurous acid, but could not obtain the salt perfectly free from starch. On finding, however, that iodine can be dissolved with slight evolution of heat in sodic or potassic sulphite, by cooling the solution after each addition of iodine as long as it is decolorised, he obtained, on evaporation at a gentle heat and allowing the solution to cool slowly, a well crystallised salt, identical in composition with the salt obtained by the action of a sulphite upon iodide of starch. Iodosulphates of the alkalies were also prepared from iodosulphuric acid, obtained by gradually adding

* Zeitsch. für Chemie, No. 15, 1870, 455. † N. Rep. Pharm., xx, 451—457.

iodine to a concentrated aqueous solution of sulphurous acid, and neutralising the acid with alkaline carbonates; and, lastly, the corresponding iodosulphates were prepared by dissolving iodine in solutions of alkaline hyposulphites, when sulphur separated according to the equation:—

$$SSO_3Na_2 + I_2 = SO_3I_2Na_2 + S.$$

The author prefers to dissolve iodine in alkaline sulphites, as being at once the easiest and most expeditious method of preparing iodosulphates. He recommends that the iodine should be added in the cold, and only in small portions at a time, in order to avoid any rise of temperature; also, that the solution of the salt should be evaporated in a cool and dark place, at a very moderate heat, and should be protected as much as possible from the action of the air.

Sodic Iodosulphate, $SO_3I_2Na_2 + 10$ aq.—This salt crystallises in colourless, long, symmetrical prisms; it has a bitter taste, which is, however, less disagreeable than that of the sulphate; it is readily soluble in water,—100 parts of water dissolve 27·5 parts of the salt at 15°; it is also very soluble in alcohol. When heated, it gives off iodine, and is converted into sodic sulphide and sulphate. Exposed to air and light, it is rapidly decomposed. A solution of the salt in water does not react alkaline, and is decomposed by a weak galvanic current into hydriodic acid, sulphuric acid, and soda. Sulphuric acid decomposes it with evolution of sulphurous anhydride and iodine vapours. Nitric acid precipitates iodine; mercuric nitrate produces a yellowish-white, silver nitrate a dirty-white, and lead acetate a white precipitate. Hydrochloric acid liberates the free acid with formation of sodic chloride. A solution of mercuric chloride produces a white precipitate, which changes to pink and red, and is soluble in excess of the reagent. Baryta-water gives a white precipitate, which dissolves almost entirely in hydrochloric acid. Cupric sulphate produces, after a time, a greenish-white; auric chloride, a very dark brownish-red precipitate; metallic gold and silver even are acted upon by a solution of sodic iodosulphate.

The author determined the composition of the salt quantitatively by converting it into sulphate, precipitating with barium chloride, and weighing as barium sulphate. The water of crystallisation was likewise determined directly; not so, however, the iodine and soda. Neither were the two other salts, the *potassic* and *ammonic iodosulphate*, which he describes, analysed. Both salts are said to be isomorphous with the sodic salt, but to be more soluble in water. Exposed to air and light, they undergo rapid decomposition.

W. V.

On some New Alloys. By A. BAUER.*

THE alloy PtPb, formerly described by the author,† is best prepared by fusing platinum with a slight excess of lead under a covering of borax-glass. Chemical combination takes place readily, and is accompanied by vivid flashes of right. The crucible should be allowed to cool slowly (by being placed in hot ashes). The alloy is then obtained in the form of a very fine crystalline reddish mass, resembling bismuth, which may be freed from excess of lead by treatment with acetic acid and exposure to air. The density of the alloy was found to be 15·736, the calculated density being 14·89,‡ from which it follows that contraction takes place when platinum and lead combine. An alloy containing two atoms of lead to one of platinum, is obtained by employing excess of lead. The alloy $PtPb_2$, differs but little from PtPb in its outward appearance.

Alloys of lead with several other metals were also prepared. Two parts of lead were fused in a crucible, and one part of mercury gradually added. The resulting amalgam was then acted upon with acetic and carbonic acids whilst exposed to air, as long as any sugar of lead and white lead was formed. It was found to contain 40·86 of lead and 59·12 of mercury, the formula Pb_2Hg_3 requiring 40·82 of Pb and 59·17 of Hg, and was obtained as a compact, crystalline, granular white mass, of specific gravity 12·49 at 17° C. The calculated density of an amalgam of Pb_2Hg_3 is 12·6085 (sp. gr. of Hg = 13·557). Hence it follows that no contraction took place. This is quite in harmony with the observations made by Crookewitt§ on amalgams of equal atoms of lead and mercury, but runs counter to the observations made by Kupffer on lead amalgams.

An alloy of lead and palladium was obtained by fusing granulated lead in a porcelain crucible, with somewhat more than one part by weight of palladium foil. Combination takes place readily and is marked by flashes of light. The product is a beautiful, crystalline, brittle, greyish-white mass, which is freed from excess of lead by acting upon it with acetic and carbonic acids. It is attacked freely, sugar of lead and white lead being formed; and on powdering it very finely and exposing it repeatedly to the action of these acids, it was noticed that palladium even dissolved in‖ acetic acid, and that the

* Deut. Chem. Ges. Ber., iv, 449—454. † Wien. Akad. Ber. iii, 836.

‡ Calculated according to the formula $100 : \left(\frac{A}{S} + \frac{A}{S'}\right)$, S and S′ representing the specific gravities of the respective metals, and A and A′ the percentage composition of the compound. § Ann. Chem. Pharm., lxviii, 290.

‖ Palladious oxide, obtained by precipitation of palladious nitrate by sodic carbonate, was found to be readily soluble in acetic acid, from which solution metallic palladium is separated on long continued boiling.

remaining alloy was of constant composition. This alloy, which has the composition Pd_3Pb, forms a steel-grey, crystalline powder, difficultly fusible, and having a specific gravity of 11·225, theory requiring 11·65. When it was used as a negative electrode in a battery of six Bunsen elements, no occlusion of hydrogen could be traced.

No alloys of lead and gold and of lead and silver could be obtained by fusing together the respective metals.

An alloy of 74·31 p. c. of copper and 25·44 p. c. of zinc, said to have been obtained accidentally in some Austrian brass-works, is mentioned by the author, which differs from the alloys of copper and zinc described by Croockewitt,* and has the formula Cu_3Zn.

W. V.

On the Spontaneous Decomposition of Potassium Bisulphite. Answer to the observations of M. Langlois. By C. Saint-Pierre.†

In a former communication‡ the author described the spontaneous decomposition which a solution of potassium bisulphite undergoes when kept in a closed vessel, sulphuric acid and trithionic acid being formed, and sulphur deposited. These results having been criticised by Langlois, the author has made fresh experiments.

A solution of the bisulphite enclosed in an assay flask in 1862, became yellowish in 1865, and in 1866 a deposit of sulphur was formed which increased until 1868, when the solution was sensibly decolorised, B. In similar flasks the author ascertained the presence of sulphuric acid and acids of the thionic series, C. As Langlois had attributed the results obtained in the former experiments to the solution being dilute, the author repeated them with a saturated solution containing undissolved crystals of the bisulphite, but with the same result, D. A saturated solution of potassium bisulphite was diluted with twice its volume of water, when the same decomposition took place as in the preceding experiment.

In conclusion, the author states that he has thus shown that the amount of dilution does not affect the reaction, the spontaneous decomposition of the potassium bisulphite taking place slowly at the ordinary temperature, with liberation of sulphur and formation of sulphuric acid and thionic acids.

C. E. G.

* Ann. Chem. Pharm., lxviii, 292. † Compt. rend., lxxiii, 749—751.
‡ Compt. rend., 12th March, 1866.

On the Hydrate of Magnesium Oxychloride. By C. BENDER.*

THE hydraulic properties of pure magnesia have long been known. Sorel found that they were intensified by the addition of a solution of magnesium chloride. It is best to take the *magnesia usta* of commerce, heat it in a Hessian crucible, and add a concentrated solution of magnesium chloride (20°—30° Baumé), so as to make a thick paste; after some hours the mass becomes dry and hard. A sample of this, exposed to the air for six months, was analysed; different portions of the mass contain different proportions of magnesium carbonate, but if this be subtracted from the analytical numbers, the mass then appears to bear the composition $MgCl_2.5MgO + 17H_2O$, which the author believes to be a chemical compound. The mass loses 3 molecules of water when dried over sulphuric acid, 6 more at 100°, and two at 150°—180°. The hydrate of magnesic chloride begins to decompose at 106°; but the above body contained the same proportion of chlorine before and after heating to 150°, showing that no decomposition of the magnesium chloride had taken place. This compound may be considered as a basic magnesium oxychloride.

By treatment with water at the ordinary temperature, magnesium chloride is removed, and after very careful washing the remaining compound, when dried over sulphuric acid, is found to correspond with the formula $MgCl_2 . 9MgO + 24H_2O$. The compound loses 9 molecules of water at 100°, and five more at 150°—180°.

If this compound be treated with boiling water for a long time, the whole of the magnesium chloride is removed, the compound remaining after drying over sulphuric acid having the composition $2MgO + 3H_2O$; it loses water at 100°, and also at 150°, when it forms $4MgO + 5H_2O$. This magnesium hydrate resembles the mineral brucite in the property that is attacked with difficulty by carbonic acid.

The author thinks that the formulæ of the first two bodies should be doubled, and that their composition should be thus expressed:—

1. $2\{MgCl_2 . MgO\} + 16H_2O + 4\{2MgO + 3H_2O\}$.
2. $\{MgCl_2 . MgO\} + 12H_2O + 4\{2MgO + 3H_2O\}$.

The author believes that magnesium may be a tetrad element, and gives as an example the hydrate obtained, $4MgO + 5H_2O$, which might be expressed by the symmetrical formula—

$$O\left\{\begin{matrix} MgH(OH)_2. \\ MgH(OH). \end{matrix}\right. \quad O\left\{\begin{matrix} MgH(OH). \\ MgH(OH)_2. \end{matrix}\right.$$

A. P

* Ann. Ch. Pharm., clix, 341—349.

Derivatives of Luteo- and Roseo-cobaltic Iodosulphate. By J. M. KROK.*

THE author has examined a large number of salts prepared directly from the above iodo-sulphates, obtained by the method previously described by Blomstrand† in this Journal.

The luteo-salts prepared from the iodo-sulphate, $Co(NH_3)_{12}I_2.2SO_4$, were the chloride, $Co(NH_3)_{12}Cl_6$, and the nitrate, $Co(NH_3)_{12}.6NO_3$, both by evaporation with the respective acids; the chlorosulphate, $Co(NH_3)_{12}Cl_2.2SO_4 + 6aq$, by the moderated action of chlorine; the chlorobiniodate, $Co(NH_3)_{12}Cl_4I_4O_{11}$, by the continued action of chlorine; and the mercury and platinum double salts, $Co(NH_6)_{12},Cl_2.2SO_4.2HgCl_2$, $Co(NH_3)_{12}Cl_6.2HgCl_2 + 3aq.$, and $Co(NH_3)_{10}Cl_2 2SO_4PtCl_2$.

From the roseo-sulphate, $Co(NH_3)_{10}S_2.2SO_4 + 2aq.$, the bromo-sulphate, $Co(NH_3)_{12}Br_2.2SO_4 + 2aq.$, the chloride, $Co(NH_3)_{12}Cl_6 + 2aq.$, the nitrate, $Co(NH_3)_{10}.6NO_3 + 2aq.$, $Co(NH_3)_{10}Cl.5NO_2 + 3aq.$, and the double salts, $Co(NH_3)_{10}Cl_2.2SO_4.2HgCl_2 + 2aq.$, $Co(NH_3)_{10}Cl_4.2NO_3.2PtCl_2$, $Co(NH_3)_{10}Cl_3.3NO_3.3HgCl_2$ were obtained.

Of the so-called purpureo-salts, the chloride, $Cl_2Co(NH_3)_{10}Cl_4$, was prepared by the action of hydrochloric acid on the iodo-sulphate. Gibbs and Genth obtained a salt from purpureo-chloride, of the composition $10NH_3.Co_2O_3.C_2O_3 + aq.$; according to them the only neutral purpureo-salt with an oxacid; but whereas in the purpureo-chloride two of the chlorine atoms seem to be more firmly fixed than the others, the author held this to be improbable, and, repeating the experiment, obtained a salt with the same properties, but of the composition $Cl_2Co(NH_3)_{10}.2C_2O_4$.

H. E. A.

Sulphites of Copper and Silver. By N. SVENSSON.‡

THE older, often contradictory, statements with reference to these compounds have been revised, and several new salts prepared.

Copper Salts.—The ordinary red salt was found to have the composition assigned to it by Rammelsberg, *i.e.*, (1) $2CuSO_3 + 5aq.$ Rogojski's§ simple cuprosum salt could not be obtained.

Potassium Double Salts.—The following were obtained:—(2) $K_2SO_3.CuSO_3.4KHSO_3 + 5aq.$; (3) $K_2SO_3.CuSO_3 + 6KHSO_3$.

Sodium Double Salts.—(4) $Na_2SO_3.CuSO_3 + 2aq.$; (5) $Na_2SO_3.CuSO_3 + 11aq.$; (6) $3Na_2SO_3.2CuSO_3 + 2aq.$; (7) $7Na_2SO_3.CuSO_3 + 19aq.$

* Deut. Chem. Ges. Ber., iv, 711, from Lund's Univ. Arsskrift.

† Page 193 of this volume.

‡ Deut. Chem. Ges. Ber., iv, 713, from Lund's Univ. Arsskr.

§ Ann. Ch. Pharm., lxxx, 256.

Ammonium Double Salts.—(8) $Am_2SO_3.CuSO_3$; (9) $Am_2SO_3.CuSO_3 + 14aq.$; (10) $5Am_2SO_3.CuSO_3 + 2aq.$; $(Am_2SO_3 + CuSO_3).(CuSO_3 + CuSO_3)$.

Silver Sulphites. — $Na_2SO_3.Ag_2SO_3 + 4aq.$; $Am_2SO_3.Ag_2SO_3$; $6Am_2SO_3.Ag_2SO_3 + 19aq.$; $3Am_2SO_3.Ag_2SO_3.4AmHSO_3 + 18aq.$

Blomstrand discusses the constitution of the above compounds at some length, representing the cuprosum sulphites as follows:—

1. $Cu\begin{matrix}O.SO.O\\O.SO.O\end{matrix}Cu$

2. $\begin{matrix}K_5.O_5.(SO)_3.O\\KH_4.O_5.(SO)_3.O\end{matrix}Cu + 5aq.$

3. $\begin{matrix}K_7.O_7.(SO)_4.O\\KH_6.O_7.(SO)_4.O\end{matrix}Cu$

4 and 8. $\begin{matrix}R.O.SO.O\\R.O.SO.O\end{matrix}Cu.$

6. $\begin{matrix}Na_5.O_5.(SO)_3.O\\Na_5.O_5.(SO)_3.O\end{matrix}Cu + 38aq.$

7. $\begin{matrix}Na_7.O_7.(SO)_4.O\\Na_7.O_7.(SO)_4.O\end{matrix}Cu + 19aq.$

9. $\begin{matrix}Am_5.O_5.(SO)_3.O\\Am_5.O_5.(SO)_3.O\end{matrix}Cu + 2aq.$

H. E. A.

On Chromate of Chromic Oxychloride. By EMIL ZETTNOW.*

WHEN potassic chlorochromate is mixed with sulphuric acid of sp. gr. 1·84, and heat applied, drops of a dark brown viscid liquid make their appearance on the sides and in the neck of the retort, beside the oxychloride. These drops do not mix with the oxychloride, but pass gradually into the receiver. They either float on the oxychloride or sink down in it, according to the amount of water they contain.

To obtain this brown compound in a state of purity, 250 grams of of potassic chlorochromate were mixed with 100 c.c. of fuming sulphuric acid, of sp. gr. 1·888, and the mixture was heated for $1\frac{1}{2}$ hours in a chloride of calcium bath, and afterwards on a sand-bath, as long as any drops of the brown compound came over. From the distillate, consisting of the oxychloride and the brown compound, the former was first removed, as far as possible, by decantation, the complete removal being effected by placing the vessel containing the distillate into a water-bath and passing a current of dry air through the liquid. Finally the substance was dried over oil of vitriol for six weeks. This process was twice repeated with the same quantity of chlorochromate, but using 100 c.c of sulphuric acid of sp. gr. 1·84, and 150 c.c. of the same acid with addition of 18 grams of dry chromic chloride, instead of the 100 c.c. fuming acid. The three portions thus prepared, marked A, B, and C respectively, amounted to 10, 8, and 15 grams. The purified and dried compound constituted a dark brown, amorphous, brittle mass, extremely deliquescent. On analysis, nothing but chromic chloride, chromic acid, and water, were detected.

* Pogg. Ann., cxliii, 328—334.

The composition of the three portions, after deduction of water, may be thus represented:—

	A.	B.	C.
Chromic acid	59·62	60·66	55·26
Chromium	16·07	14·60	16·25
Chlorine	22·31	23·24	26·98
Oxygen	2·00	1·51	1·51

The compound therefore appears to be a chromate of the oxychloride, of somewhat variable composition. On the assumption that water does not enter into the constitution of the salt, the compounds A and B may be thus formulated: $Cr_2Cl_4O.4CrO_3$; and compound C as $Cr_{12}Cl_{15}O_3.22CrO_3$.

Thorpe, in a recent communication to the Chemical News (Nov. 10, p. 219), has pointed out that the compound just described is identical with the solid chromium oxychloride which he described two years ago (Proc. of the Lit. and Phil. Soc. of Manchester, Nov. 2, 1869) as obtained by heating chromyl dichloride in a sealed tube, and to which, for reasons given in the memoir just quoted, he assigned the formula $ClCrO_2.Cr''O,CrO_2Cl$. The two compounds agree almost exactly in physical properties, and very nearly in composition, as the following comparison will show:—

	Analysis.		Calculation.	
	Thorpe.	Zettnow (A,B)	Thorpe.	Zettnow.
Chlorine	21·06	22·31	21·86	21·42
Chromium	48·91	47·28	48·54	47·23

A. D.

Mineralogical Chemistry.

Analysis of a Rock and some Ochreous Deposits from the Mineral Springs of the Teplitz Basin. By J. STINGL.*

I. Quartz-porphyry from Teplitz, sp. gr. 2·567.

II. Ochreous deposit from the Hügelquelle of the new bath at Schœnau, near Teplitz, sp. gr. 2·73.

III. Dark reddish-brown ochreous deposit from the Steinbad spring at Teplitz.

IV. Calcareous deposit from the Hügelquelle of the new bath at Schœnau, sp. gr. 2·698.

* Deut. Chem. Ges. Ber., iv, 454—456; Wien. Akad. Ber., lxiii [2], 325—328.

Constituents.	Quartz Porphyry. I.	Ochreous deposits. II.		III.		Calcareous deposit, IV.	
		Soluble in HCl.	Insoluble.	Soluble in HCl.	Insoluble.	Soluble in HCl.	Insoluble.
Silica	75·47	..	9·44	..	65·61	..	16
Carbonic anhydride	..	34·84	..	·85	..	41·50	..
Alumina	15·07	..	1·06	..	3·18	·25	..
Ferric oxide	3·86	2·24	·42	20·20	1·30	2·49	..
Manganous oxide	..	5·34	..	1·52	..	..	..
Lime	·95	43·77	trace	trace	..	52·50	..
Magnesia	·63	..	..	..	..	trace	..
Potash	1·85	..	traces	traces	traces	..	..
Soda	·51	..				1·75	..
Lithia	..	..	..	..	..	trace	..
Water	1·43	3·11	..	7·12	..	1·29	..
	99·77	100·22		99·78		99·94	

W. V.

On the Composition of Epidote. By A. KENNGOTT.*

IN this paper the author discusses all the published analyses of epidote, and comes to the conclusion that, with the exception of a few of doubtful character, they may all be included in the general formula—

$$CaO.H_2O + 3(CaO.SiO_2 + Al_2O_3.SiO_2),$$

the alumina being more or less replaced by ferric oxide, and the lime to a small extent by magnesia; the presence of the magnesia appears, however, to be due, in many cases at least, to foreign minerals imbedded in the epidote. In some of the analyses, the iron is calculated partly as ferrous oxide; this, however, Kenngott reckons also as ferric oxide, and regards it as taking the place of an equivalent quantity of alumina.

The least ferruginous epidotes are those from Switzerland and the Formazza valley; in these the ratio of alumina to ferric oxide $Al_2O_3 : Fe_2O_3 :: 5 : 1$. In the epidotes from Bourg d'Oisans in Dauphiny, Traversella in Piedmont, Arendal in Norway, and Penig in Saxony, the ratio is $Al_2O_3 : Fe_2O_3 :: 2 : 1$.

H. W.

* Jahrbuch für Mineralogie, 1871, 449—459.

Ilsemannite, a Native Molybdenum Salt. by H. Höfer.*

The author gives this name to native molybdic molybdate, $MoO_2.4MoO_3$, occurring at Bleiberg in Carinthia, as a bluish-black to black, mostly earthy or cryptocrystalline deposit, between groups of crystals of barium sulphate. It is soluble in water, and acquires a deeper blue colour by exposure to the air. When purified from gypsum and other admixtures by repeated solution in water and evaporation, it dissolves in water with a splendid dark blue colour, and the solution treated with hydrogen sulphide, deposits a blue precipitate without losing much of its own colour. The author attributes its formation to the action of sulphuric acid on native lead molybdate (wulfenite); many samples of the native mineral indeed were found to contain free sulphuric acid, together with the sulphates of barium and calcium.

H. W.

Hydrated Sodium Chloride from Etna. By. A. Kenngott.†

Silvestri in 1870 analysed a mixture of chloride and carbonate of sodium occurring in the Etna lavas, with the following results:—

	NaCl.	KCl.	Na_2CO_3.	Na_2SO_4.	H_2O.	
1	50·19	0·50	11·12	1·13	37·06	= 100
2	63·02	0·27	6·19	trace	30·22	= 100
3	76·01	0·03	2·11	0·75	21·10	= 100

Regarding the carbonate as monohydrated (soda) and the sulphate as decahydrated (mirabilite), the composition of these mixtures may be represented as follows:—

	Na_2SO_3	+ H_2O.	Na_2SO_4	+ 10 H_2O.	NaCl.	KCl.	H_2O.
1	11·12	18·88	1·13	1·43	50·19	0·50	16·75
2	6·49	11·02	trace	trace	63·02	0·27	19·20
3	2·11	3·58	0·75	0·95	76·01	0·03	16·57

Analysis 1 gives 8·58 NaCl, 0·07 KCl (= 8·65) and 9·31 H_2O; analysis 2 gives 10·77 NaCl, 0·04 KCl(= 10·81), and 10·67 H_2O, both agreeing with the formula $NaCl.H_2O$.

In the third analysis the quantity of water is below that required by the ratio 1 : 1, whence it may be inferred that the hydrate $NaCl.H_2O$ was mixed with a certain quantity of anhydrous sodium chloride. It is worthy of remark that the sodium chloride exists in the fumarole vapour in the form of hydrate, and is deposited as such; and that the

* Jahrbuch für Mineralogie, 1871, 566. † Jahrbuch für Mineralogie, 1871, 500.

anhydrous chloride, when it occurs, appears to result from the decomposition of this hydrate, as indicated by the third analysis.

H. W.

Iridescent Laminæ in Hypersthene. By BERNHARD KOSMANN.*

THE author has shown by microscopical examination that the iridescent laminæ enclosed in the hypersthene of St. Paul's Island belong to the rhombic system, and exhibit the forms and combinations of Brookite. He also finds by chemical analysis that this mineral contains 0·46 p.c. titanic acid. He supposes that the crystalline laminæ of this substance were suspended in the solution from which the hypersthene was deposited, and arranged themselves in accordance with the direction of the layers of the hypersthene, and with the relations of elasticity required by its crystallisation.

Similar iridescent laminæ are found embedded (together with other crystals), in labradorite, and Schrauf (*Jahrb. f. Min.* 1871, 743) finds that they are of two kinds, distinguished from one another by their form and position. The laminæ of the one system have for the most part a rectangular or often square transverse section, and lie parallel to a hypothetical labradorite face $\infty P \breve{\tfrac{29}{4}}$, while those of the second system exhibit elongated and mostly irregular forms, and lie parallel to a hypothetical labradorite face $\infty P' \breve{\tfrac{31}{4}}$. The arrangement of the two systems of laminæ is moreover a regular consequence of the secondary cleavage of the labradorite, resulting from the other imbedded crystals.

H. W.

Rosthornite, a new Fossil Resin. By HANNS HÖFER.†

THIS resin occurs in the coal-beds of the Sonnberg, near Guttaring in Carinthia. It has a fatty lustre, a brown colour with garnet-red lustre, wine-yellow by transmitted light, especially in splinters, and a light-brown to orange-yellow streak. It is brittle and may be scratched with the nail. Sp. gr. = 1·076. When heated in the air, it gives off white vapours having an aromatic odour, and burns with a deep yellow smoky flame, without leaving any residue. At 96° it begins to melt to a viscid, brown-red mass which throws up bubbles at 160°, and emits white vapours from 215° to 225°, at which latter temperature the mass becomes mobile, assumes a dark purple-red colour, and emits a fetid gaseous mixture, but does not give off succinic acid. When fused with alkaline carbonates, it does not exhibit

* Jahrbuch für Mineralogie, 1871, 501.

† Jahrbuch für Mineralogie, 1871, 561—566.

any trace of sulphur, although that element is present in the coal in the immediate neighbourhood of the resin. Rosthornite is not altered by dilute nitric acid, by potash-ley or by alcohol, either in the cold or on boiling; in warm ether, however, it dissolves partially, forming a turbid wine-yellow solution, and leaving a white tumefied residue. In cold turpentine-oil it remains unaltered, but hot turpentine-oil dissolves the pure resin almost entirely, leaving only a small quantity of dark-coloured matter (enclosed particles of coal). It swells slightly in cold and dissolves partially in hot petroleum. In benzol it dissolves at ordinary temperatures, forming a clear dark wine-yellow liquid.

Rosthornite, in its physical characters, bears considerable resemblance to jaulingite and pyroretinite, but in chemical composition it approaches more nearly to euosmite, and still more to the fossil resin of Girona, near Bucaramanga in New Granada, as will be seen from the following comparison:—

	Rosthornite.	Jaulingite.	Euosmite.	Girona resin.
Carbon	84·42	74·43	81·89	82·7
Hydrogen	11·01	9·04	11·73	10·8
Oxygen	4·57	16·53	6·38	6·5
	100·00	100·00	100·00	100·0

Euosmite is distinguished from rosthornite by its strong odour of camphor and rosemary, by its easy and complete solubility in alcohol and ether, and by the deep yellow colour which it imparts to potash-ley, &c. Pyroretinite also differs from rosthornite in its behaviour to solvents, and moreover contains 10 p. c. oxygen. Girona or Bucaramanga resin, which occurs in auriferous porphyritic alluvians, resembles rosthornite in its behaviour to alcohol and ether, but is transparent, pale-yellow, and very much like amber in its physical characters.

Rosthornite, therefore, cannot be included either physically or chemically in the succinite group, or in that of retinite (80·4 C.; 10·7 H.; 8·7 O.), neither on chemical grounds can it be referred to the ixolite group, to which jaulingite belongs. It appears rather to form a type of solid resins rich in carbon and poor in oxygen.

H. W.

Beyrichite and Millerite. By K. T. LIEBE.*

BEYRICHITE is a native sulphide of nickel, lately obtained from a mine in the Westerwald. It forms radiate groups of macled crystals, made up of prisms about 70 mm. long, and 8 mm. thick, some of which have a helicoïdal curvature. The prismatic groups have mostly a single end-face inclined at 81° to the vertical axis. A second, but somewhat rarely occurring end-face, forms with the first a dome-like combination, with an angle of 144°, corresponding to the angle of the terminal edges of Millerite. Cleavage moderately distinct, parallel to the first mentioned end-face.

The mineral belongs to the family of the glances, rather than to that of the pyrites. It is very tough, but moderately impressionable to the point of a knife. Hardness, about 3·2 to 3·3. Sp. gr., 4·7. Colour, red-grey, with faint metallic lustre, stronger on the cleavage faces. When heated in a tube, it decrepitates, and at a dull red heat, gives off sulphur, without fusion, and is thereby converted into a pyrites, having a dark pinchbeck-brown tarnish on the surface, speiss-yellow to brass yellow internally, harder and more brittle than the original mineral. On charcoal, beyrichite melts easily and quietly, with evolution of sulphurous acid, to a strongly magnetic bead, having a brass-yellow colour internally. It gives the nickel reaction with borax and phosphorus-salt, and dissolves easily in hydrochloric acid, especially on addition of nitric acid, forming an emerald-green solution. Pure specimens yield by analysis 42·86 p. c. sulphur, 2·70 iron, and 54·23 nickel. If the iron be supposed to replace an equivalent quantity of nickel, these numbers lead to the formula Ni_5S_7 or $3NiS.2NiS_2$ (calc. 43·21 S., and 56·79 Ni). The presence of the iron may, however, be due to the admixture of iron pyrites, and in that case the composition of beyrichite may be represented by the formula, $2NiS.NiS_2$.

Beyrichite is accompanied by a pyrites having a deep brass-yellow to speiss-yellow colour, often variegated on the surface, which coats the beyrichite crystals in extremely thin laminæ, or more rarely in dendritic or thin crystalline forms, often penetrating them in the direction of the cleavage-planes, in the form of sharply separated lamellæ, sometimes to the complete displacement of the beyrichite. This mineral is Millerite or capillary pyrites, having a sp. gr. of 5·7 to 5·9, hardness between 3·6 and 3·8, and containing 35·27 p. c. S, 1·16 Fe, and 63·41 Ni, agreeing, therefore, with the formula N.S.

Beyrichite, as appears from the facility with which it gives off sulphur when heated, is very easily converted into Millerite, a circumstance which may perhaps account for the great variations in the statements

* Jahrbuch für Mineralogie, 1871, 840.

relating to the specific gravity and other properties of the latter. Liebe finds the specific gravity of millerite to vary between 5·7 and 5·9 (Dana gives 5·25—5·65); a specimen from the Joachimsthal was found by Kenngott to have the sp. gr. 4·601, which is not far from that of beyrichite. These diversities may be due either to the presence of beyrichite enclosed in the capillary pyrites, or to the different conditions under which the transformation of beyrichite into millerite takes place. Beyrichite is, in fact, converted into Millerite by taking up nickel from the vein-water, and the more compact and less porous the structure of the beyrichite, the denser and heavier will be the Millerite formed from it.

H. W.

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*Mineralogical Notices.**

Felspar from Blansko in Moravia. By H. Wieser.—The syenite of Blansko contains a decomposed plagioclase, in which distinct crystals of orthoclase are perceptible. The analysis of this felspar gave—

SiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	
45·49	trace	22·86	1·69	2·04	1·76	21·81	trace	trace	3·08	1·84	=100·57

—Plagioclase is therefore a calcio-sodic felspar.

Amounts of Barium and Manganese in certain Minerals. By L. Raab.—The author concludes, from the examination of a considerable number of minerals, that very few of the silicates at present known, contain barium; this element is, however, present in the stilbite of Iceland. Four chromites were found to contain manganese, the proportion of which in the Siberian and Norwegian chromites is greater than in those from the Ural and from Texas. Five magnetites were found to contain from 1·08 to 1·53 p. c. manganese. As fluorine forms a volatile compound with iron, the decomposition of minerals with hydrofluoric acid appears to be well adapted for the estimation of manganese, but may lead to errors in the estimation of the iron and silica.

Analysis of Efflorescences from Lago d'Ansanto. By H. Wieser.—These efflorescences, which form a coating on the mud, were found to have the following composition:—

Insoluble in water, 1·99.		Soluble in water, 81·21				Water, 18·66.		
FeO.	Al_2O_3.	SO_3.	FeO.	Al_2O_3.	Na_2O.	at 163°.	on ignition.	
0·68	1·31	53·00	9·55	16·16	2·50	4·74	13·92	= 101·86

* Jahrbuch für Mineralogie, 1871, 517, 521, and 637—642.

Analysis of Nadorite.—This species, first established by Flajolot, has been analysed by Pisani, who finds it to contain 37·40 p. c. Sb_2O_3, 27·60 PbO, 26·27 Pb, and 9·00 Cl, leading to the formula $PbO.Sb_2O_3 + PbCl_2$. The presence of chlorine in an antimony mineral is especially interesting. Flajolot, on re-examination of the mineral, has also found chlorine in it. His analysis gives 51·60 Sb, 32·25 Pb, 8·00 O, and 8·85 Cl (= 100·70).

Analysis of Siliceous Calamine from Scharley, in Upper Silesia. By H. WIESER.—Implanted, fan-shaped groups of white crystals, having a sp. gr. of 3·36.

SiO_2.	P_2O_5.	ZnO.	Fe_2O_3.	Na_2O.	H_2O.	
24·36	0·51	64·83	0·72	0·73	8·46	= 99·61.

Phosphoric acid has also been found by Schnabel in the siliceous calamine of Cumillas, near Santander in Spain.

Monzonite, a new Mineral Species. By F. v. KOBELL.—This mineral, from the Monte Monzoni in the Fassa Valley, near the small lake of Le Selle, is compact and occurs in fragments. Hardness = 16; sp. gr. = 3. Fracture, splintery to imperfectly conchoïdal. Colour, light green, like that of many green hornstones. Slightly translucent on the edges. Melts easily before the blowpipe to a shining greyish-green glass. Gives off a little water when heated in a tube. Insoluble in hydrochloric and sulphuric acid, but dissolves in strong aqueous phosphoric acid. Analysis gave—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	
62·60	17·10	9·00	9·65	2·10	6·60	1·90	1·50	= 100·45

leading to the formula $12(R''O.SiO_2) + 4Al_2O_3.9SiO_2$. The mineral, when examined in a thin slice under the microscope, shows no signs of mixed constitution, and may therefore be regarded as a distinct species.

Abnormal Crystals of Sodium Chloride. By F. v. KOBELL.—The author has carefully re-examined the crystals of rock salt from Berchtesgaden, which exhibit a remarkable partial development of faces, resembling a rhombohedral combination, in order to discover whether this abnormal development is due to the presence of foreign substances; but he found nothing but a small trace of potassium chloride.

Ullmannite from the Rinkenberg in Carinthia. By M. v. LILL.—This mineral, which occurs embedded in a rock consisting of talcose clay-slate and crystalline dolomite, exhibits, when crystallised, the combination $\infty O\infty . \infty O$; very distinct cubic cleavage; sp. gr. = 6·63; tin-white to steel-grey colour. Analysis gave 15·28 p. c. sulphur, 56·07 antimony, 27·50 nickel, and 0·94 arsenic (= 99·79). A small part of the antimony is replaced by arsenic. The mineral is also found at the Löling-Hüttenberger Erzberg and Waldenstein in Carinthia.

Trinkerite from Gams near Theglaw in Styria. By J. NIEDZWIEDZKI.—This species, described by G. Tschermak (*Jahrbuch.* 1870, 799), occurs in flat, elongated nodules in a black-grey marl impregnated with carbonaceous particles. Hardness = 2; specific gravity = 1·032; fracture, flat conchoïdal; colour, yellowish to reddish-brown: lustre, fatty. Analysis gave 81·9 p. c. carbon, 10·9 hydrogen, 4·1 sulphur, and 3·1 oxygen (= 99), agreeing with that of the trinkerite of Carpano.

Occurrence of Websterite near Brighton. By S. PERCEVAL.—Websterite (aluminite) forms a layer in the chalk about 3 feet thick, and probably filling a cleft; above it is a ferruginous clay with nodules of limonite, flint, and isolated crystals of gypsum. The websterite is of very variable constitution, sometimes in the form of the finest white powder, appearing under the microscope as an aggregate of extremely fine crystals, sometimes in compact nodular masses resembling meerschaum.

Kieserite from the Hallstatter Salzberg. By H. WIESER.—This kieserite is of distinctly crystalline texture, yellow colour, sp. gr. 2·56451, and contains—

SO_3.	MgO.	FeO.	Na_2O.	Cl.	H_2O.
57·87	28·89	0·05	0·05	0·06	13·24 = 100·16

Identity of Amblystegite with Hypersthene. By G. VOM RATH.—The crystals of amblystegite (*Jahrbuch.* 1870, 345) agree very nearly with those of the hypersthene or bronzite determined by von Lang in the meteorites of Breitenbach, the face $\frac{1}{4}P\breve{\infty}$ of amblystegite being alone wanting in the more numerously faced hypersthene of Breitenbach. By the discovery of hypersthene crystals in the pallasite of Breitenbach, and in the sanidin-bombs of Lake Laach, the number of silicates common to meteorites and to terrestrial minerals, is increased to five.

H. W.

Occurrence of Lithia-mica in the Fichtelgebirge. By F. SANDBERGER.*

On the Crystalline form of Lead Dithionate, and the Law of the Trigonal Pyramids in Circular Polarising Substances. By A. BREZINA.†

Crystallographical Notices.‡

On Anhydrite. By F. HESSENBERG.—*On the Gypsum of Wasenweiler.* By F. HESSENBERG.—*Occurrence of Babingbonite at Herbornseelbach in Nassau.* By G. VOM RATH.—*On the Ilvaite of Nassau.* By G. VOM RATH.—*Atacamite Crystals from South Australia.* By F. ZEPHAROVICH.—*New Faces of Apatite.* By A. SCHRAUF.—*Apatite from Poloma, in Hungary.* By A. SCHRAUF.

Meteoric Iron from the Desert of Atacama (1870). By E. LUDWIG.§

THE fragments of this meteoric iron submitted to the author were polished on the surface, perfectly free from oxide, soluble without residue in warm nitric acid. One of the larger fragments was found to contain iron, cobalt, nickel, copper (a trace), and phosphorus; a smaller fragment contained, in addition, a very small quantity of sulphur. Quantitative analysis gave as a mean result—

Fe.	Ni.	Co.	Cu.	P.	
91·53	7·14	0·41	trace	0·45	= 99·53

H. W.

Notice of the Meteoric Stone of Searsmont, Maine. By CHARLES U. SHEPARD.‖

IMMEDIATELY after the fall of this large meteoric stone the author obtained possession of a portion of it weighing about two pounds. The original mass would appear to have presented an oval sub-conical outline, the exterior being covered with a thick crust of at least one-sixteenth of an inch in thickness. Its colour is bluish-white, and remarkably uniform, but is slightly stained in one or two places with peroxide of iron. More than one-half of the meteorite is composed of small, rounded, translucent grains, vitreous in lustre, and rarely exceeding a

* Jahrbuch für Mineralogie, 1871, 642. † Ibid., 643. ‡ Ibid., 510—517.
§ Wien. Akad. Ber., lxiii [2], 323. ‖ Am. J. of Sci. [3], 133—136, and 200.

mustard-seed in size. Between these, and often partially coating them, is a fine-grained white, or greyish-white, mineral, which is supposed to be chladnite; it constitutes about one-fourth of the stone, is without visible crystalline structure, and rather loosely coherent. Minute points of bright meteoric iron are very thickly scattered throughout the mass, and a few grains of troïlite are visible. In one spot only a peculiar blackish substance of small dimensions was noticed, which on being touched with the point of a knife was found to be soft, and to leave a bright metallic streak; it was probably a plumbaginous aggregate.

In appearance, especially in the well marked character of its granules, this stone closely resembles the Aussum (France) meteorite of December, 1858, while in the thickness and general character of the crust, it also corresponds to the celebrated Mauerkirchen stone of 1768.

The specimen forming the subject of the present notice was analysed by Prof. Lawrence Smith, with the following results:—Specific gravity, 3·701; stony matter, 85·38 p. c.; nickeliferous iron, 14·62 p. c. The iron afforded:—Iron, 90·02; nickel, 9·05; cobalt, 0·43.

The stony portion treated with a mixture of hydrochloric and nitric acids, gave:—52·3 p. c. soluble in acid, and 47·7 insoluble.

Both the soluble and insoluble portions consisted essentially of double silicates of iron and magnesia, the soluble part being classed as an olivine, while the insoluble was considered to be either bronzite or eustatite.

The proximate composition of the stone would then be—

Nickeliferous iron	14·63
Magnetic pyrites	3·06
Olivine	43·04
Bronzite, with a little orthoclase and chrome iron	39·27

J. W.

On the Artesian Well of Rochefort. By M. Roux.*

The water of this well rises from below the sandstone at a depth of 857 metres. This is the deepest artesian boring hitherto effected, being deeper than that of Grenelle, and of Passy, by upwards of 150 metres. The water flows at the rate of from 2½ to 3 litres per second, and has a mean temperature of about 41°. On standing in contact with the air, it loses carbonic acid and nitrogen, and becomes turbid, owing to the decomposition of the ferrous carbonate which it holds in solution. One litre of the water (sp. gr. 1·0053) contains—

* Compt. rend., lxxiii, 910—913.

	c.c	grm.
Nitrogen (at 0° and 760 mm.)	17·11	0·00504
Carbon dioxide (at 0° and 760 mm.)	2·54	
Sulphuretted hydrogen		0·00067
Sodium sulphate		2·55005
Calcium sulphate		1·80956
Magnesium sulphate		0·46560
Sodium chloride		0·77894
Magnesium chloride		0·03155
Ammonium chloride		0·00968
Sodium bromide		0·00392
Sodium iodide		0·00113
Calcium carbonate		0·11057
Magnesium carbonate		0·02699
Ferrous carbonate		0·05066
Manganous carbonate		0·00015
Ferrous arseniate		0·00067
Potassium silicate		0·00421
Aluminium silicate		0·00720
Lithium silicate		traces
Ferrous phosphate		traces
Copper		traces
Organic matter (crenic and apocrenic acids)		0·00067
Water in combination		0·10200
Loss		0·01000
Calcium chloride		0·01720
Total		5·98646*

Observations on the temperature of the earth made during the boring do not accord with those formerly obtained at Grenelle.

The indications were as follows:—

Depth.	Rochefort.	Grenelle.
325 m.	21·0°	20·7°
462 m.	27·0°	24·85°
554 m.	36·5°	27·63°
669 m.	41·2°	31·12°

These observations confirm those of Walferdin, according to whom the law deduced by Fourier and Cordier is not absolutely correct, since from 550 to 800 metres 1° C. corresponds only to 23·90 metres. During the boring it was observed that the instruments became strongly mag-

* In original 5·98606.

netic, and on passing the blade of a knife over one extremity of the rod, it acted on the needle and attracted iron filings.

T. E. T.

Organic Chemistry.

On a Paraffin having a High Melting Point. By JOHN GALLETLY.*

IN manufacturing paraffin from Boghead coal, the final part of the crude oil condenser was found to contain a black, tarry matter, besides the naphtha. This nearly solid matter, when boiled with naphtha, yields a mass of a dark-brown colour (not further examined), insoluble in nearly all reagents, which dissolves bituminous bodies, and a solution which solidifies on cooling after filtration. The cooled mass when pressed in cloths, yields the crude hydrocarbon under notice, which can be purified by repeated crystallisation from naphtha. When freed from naphtha by blowing steam through it, it presents the appearance of hard yellow cakes, resembling beeswax, but more translucent. Its melting point is 80°. This it attains after the first few crystallisations, and it does not become altered after the crystallisation is repeated. It thus seems to be separated from the paraffins accompanying it in the crude oil by a considerable gap. The highest of these, after more than a dozen crystallisations, of which the last made little alteration, had a melting point of 65·5°; the original material melting at 56°.

The elementary composition of this paraffin is sensibly the same as that of other paraffins, and of ethylene.†

	Paraffin 80° C.	Ethylene.	Paraffin 52° C.
Carbon	85·2	85·7	85·45
Hydrogen	14·4	14·3	15·4

It boils at a point not far short of a red heat, suffering a partial decomposition at the same time, about one-half being converted into liquid hydrocarbons.

By the numbers given in a short table, it is shown that the solubility of the paraffins in commercial benzol, decreases very rapidly as their melting point rises, *e.g.*, 100 c.c. benzene at 18° dissolves 133 grms. of paraffin melting at 35°, but only 0·1 grm. of that melting at 80°.

The densities of the paraffins rises with their melting points. The

* Chem. News, xxiv, 187.

† A paraffin = $C_{27}H_{56}$ contains 85·26 per cent. carbon.—C. H. G.

following numbers were all obtained with paraffins from Boghead coal:—

Melting point.	Specific gravity.
32·0 C.	·8236
39·0	·8480
40·5	·8520
53·3	·9110
53·3	·9090
58·0	·9243
59·0	·9248
80·0	·9400

Picric acid forms no compound with this paraffin, but hot sulphuric acid converts it into a greasy black mass, resembling drawing chalk. Chlorine converts it very rapidly into a black oily mass which decomposed on distillation.

Heated with nitric acid (sp. gr. 1·4), the 80° paraffin is converted in an hour or two chiefly into nitro-compounds, which are readily soluble in caustic alkalies.

C. H. G.

On Isodinaphthyl. By WATSON SMITH.

THIS compound, isomeric with Lossen's dinaphthyl, is obtained, together with hydrogen, by passing the vapour of naphthalene through an iron tube heated to bright redness:

$$2C_{10}H_8 = (C_{10}H_7)_2 + H_2.$$

The naphthalene collected in the receiver has a dark-brown colour, and, when re-distilled from a retort, always leaves a minute quantity of liquid boiling at a temperature above 350°; and by repeating the distillation a certain number of times, a quantity of this substance—which consists of impure isodinaphthyl—may be obtained sufficient for further treatment. It is purified by first distilling off the small quantity of naphthalene which it contains, and then distilling over the body itself, the temperature rapidly rising from 220°, below which the naphthalene comes over, to above 360°. A minute quantity of pitch is to be left in the retort. The solid, hard, yellowish substance is now crushed in a mortar with shale-spirit, and made into a thin homogeneous paste, then washed repeatedly on a filter with the spirit, drained, pressed in blotting-paper, and dried at a temperature fully sufficient to volatilise the spirit. By this washing it is freed from a small quantity of a resinous body, and from a lemon-yellow substance. These wash-liquors all exhibit blue fluorescence. The dried substance

is finally sublimed at as low a temperature as possible, and is then obtained as a faintly yellowish-white inodorous powder. This sublimate, by very careful and slow sublimation may also be obtained in delicate little plates. When possessing the faintest yellow tint, it imparts a beautiful and delicate-blue fluorescence to any solvent used. When a very high temperature has been used (a white heat), the substance obtained is always more largely contaminated with the resinous and lemon-yellow bodies, and on careful sublimation the first portions subliming are almost colourless, but the further the sublimation is carried on, the deeper is the yellow tint of the product. A small quantity of the latter portions of a sublimation-product of a sulphur-yellow colour, when warmed with concentrated sulphuric acid, yields a very fine purple solution on further heating, passing into an indigo and then to a dull green tint. This reaction is mentioned by Liebermann as characteristic of *chrysene;* it is probable, therefore, that chrysene is present in this yellow substance.

With a quantity of the pure re-sublimed substance the following results were obtained :—

No red or brown compound is formed with a benzol-solution of picric acid. The more thoroughly the substance is purified, the less is the fluorescence imparted to solvents.

The *subliming point* of isodinaphthyl lies considerably below its boiling point. Treated with two parts of potassium bichromate and sulphuric acid, it is oxidised at once with extreme energy. From the oxidation-product obtained, no colour, nor any substance bearing any resemblance to alizarin, could be obtained. Cold sulphuric acid is without action on this body, but when heated, the acid slowly dissolves it, when, if it be quite pure, a very faint purplish-tinted solution is obtained; if, however, it contains a trace of the yellow body mentioned before, a violet or purple solution is formed, becoming green and then reddish-brown on further heating. Hot nitric acid oxidises it, with liberation of nitrous fumes, and forming in the hot fluid heavy oily drops; these on further heating dissolve in the acid, and a clear solution is obtained. On pouring into water, the nitro-compound is precipitated abundantly in a light-yellow, flocular form. Chlorine has no action upon it, when passed over it, in a glass tube, and even on warming. When it is treated with bromine in the cold, a brominated compound is formed with very energetic action.

Comparative behaviour of Di-naphthyl and Iso-dinaphthyl with Solvents, &c.

Solvents.	Lossen's Di-naphthyl.	Iso-dinaphthyl.	
	Solubility, crystalline form, &c.	Solubility.	Crystalline form, &c.
Proof spirit.....	..	Scarcely at all soluble, even on boiling with excess.	On cooling, a few plates separate out.
Ether	More soluble than in alcohol.	Very slightly; less than in alcohol.	In plates.
Absolute alcohol	Less soluble than in ether, separates in moss-like clusters.	Slightly in the cold; soluble on boiling.	Beautiful rhomboïdal plates, which, on drying, overlap, and present a beautiful silky appearance. They possess a very faint delicate greenish colour.
Methylated spirit	..	Rather more soluble.	
Wood-spirit	From ether-alcohol mixture, crystallises in octahedrons.	..	
Light petroleum spirit, sp. gr. = 710	..	Still more soluble than in the above.	Rhomboidal plates.
Light shale-spirit, sp. gr. = 737.	..	Rather more soluble than in petroleum spirit.	
Carbon tetrachloride..	..	Not quite so soluble as in benzol.	Do.
Benzol.....	About the same as in alcohol.	Sparingly in the cold, freely in the hot fluid.	Fine large fluorescent plates; on drying, a silky laminated appearance.
Carbonic disulphide ..	Easily soluble.	Easily soluble, even in the cold.	In plates.
Oil of turpentine	..	Vey easily soluble.	Delicate white lance-shaped crystals.
	Melting point = 154°C. Boiling point = over 360° C.	Melting point = 204° C. Boiling point = over 360° C.	

W. S.

On the Oxidation-products of Essential Oil of Orange-peel (Portugal). By C. R. A. Wright and Charles H. Piesse.*

Soubeiran and Capitaine, also Dr. Gladstone, have shown that the essential oil of orange-peel consists principally of a hydrocarbon, hesperidene, $C_{10}H_{16}$, boiling at 174°. The authors have examined a specimen of essence believed to be perfectly genuine, and find that the crude substance begins to boil at 175°, 97·8 per cent. of the oil being volatile below 180°; the remaining 2·8 per cent. is a soft non-volatile, yellow resin, inodorous when perfectly free from hesperidene, but slightly soluble in cold or hot alcohol, and of a bitter, aro-

* British Association Reports, 1871; Chem. News, xxiv, 147.

matic taste. On combustion this gave numbers agreeing with those required for the formula $C_{20}H_{30}O_3$, the substance containing no nitrogen.

On redistillation of the volatile portion over sodium, scarcely any action ensues, the whole being volatile between 175° and 177° (uncorrected). Concentrated nitric acid acts violently on the hydrocarbon; diluted acid less energetically, a brown resin being produced together with much oxalic and carbonic acids. By the further action of nitric acid on the brown resin, a yellow resin is produced, containing less carbon and hydrogen in 100 parts. Each resin gave on analysis numbers compatible with those required for substances derived from $C_{10}H_{16}$, by addition of oxygen and replacement of hydrogen by NO_2, nitrogen being found in each.

By boiling *per ascensum* for some hours with solution of potassium dichromate and sulphuric acid sufficient to saturate the metals present in that salt, there are produced carbonic and acetic acids, and the portion of hydrocarbon unacted on contains a small quantity of a liquid of higher boiling point than the original hesperidene. On treating this regained hesperidene with the chromic liquor, acetic acid is again produced from this regained hesperidene; the acetic acid was analysed as barium and silver salts, traces of formic acid and apparently of some volatile acid of higher molecular weight than acetic being also present.

From this production of acetic acid, the authors consider that the formula $\begin{array}{c} CH.CH_3 \\ \| \\ (C_8H_{12})'' \end{array}$ may express partially the grouping of the constituent carbon atoms in hesperidene. Further experiments in elucidation of this structure (and that of other similar substances) are in progress. C. R. A. W.

Further Observations on the so-called "First Runnings" from the Alcohol Manufacture. By A. Kekulé.*

The presence of aldehyde in the "first runnings" obtained in the manufacture of alcohol from the sugar-beet has long been known. The results of an extended investigation of these runnings has also lately been published by Kraemer and Pinner, who also note the presence of acetal in considerable quantity.

Kekulé mentions having received a letter in 1870 from H. Weinzierl, chemist to the Pommeranian sugar refinery at Stettin, stating that the latter had been engaged since 1866 in the investigation of the first runnings; that he had observed, on rectifying the more volatile portion, which consisted chiefly of aldehyde, that the fraction boiling at 50°—70° deposited white crystalline needles when cooled to − 8°. He also noticed that the distillate often became warm spontaneously, and

* Deut. Chem. Ges. Ber., iv, 718.

even boiled, just as described by Kekulé and Zincke in their communication on chloracetene. He consequently forwarded his products to Professor Kekulé.

Examination soon showed that the white crystals were, as Weinzierl had already supposed, metaldehyde, the liquid being chiefly aldehyde. On rectification a spontaneous heating of the distillate was not observed, but a considerable quantity of paraldehyde was isolated from the portion which Weinzierl had collected between 40°—60°.

These observations seem to lead to the conclusion that the fresh runnings contain, besides aldehyde, a volatile substance capable of modifying the aldehyde in the same manner as hydrochloric acid, carbonyl chloride, etc. This, in Weinzierl's experiments, in the one case, where the distillate was well cooled, had caused the formation of metaldehyde; and in the other, where it was but slightly cooled, the spontaneous heating and formation of paraldehyde. The nature of this ferment-like substance could not be determined by direct experiment, but there was a probability that some oxide of nitrogen might have had this action, and, in fact, experiment showed that even traces of nitric acid, nitric peroxide, or nitrous acid exerted upon aldehyde a modifying action similar to that of hydrochloric acid, carbonyl chloride, &c.

Kekulé questions whether the body which Kraemer and Pinner described as acetal was not paraldehyde. He is also inclined to attribute the formation of aldehyde, not to direct oxidation on the carbon filters—Kraemer and Pinner's view—but to the oxidising action of the nitrates, present in considerable quantity in the liquors fermented, which, when the so-called nitrous fermentation sets in, are reduced at the expense of the alcohol.

In reply to the above, Kraemer and Pinner* state that they omitted specially to refer to the presence of metaldehyde and paraldehyde, both of which they obtained, the latter in considerable quantity, because they considered the formation of these bodies a matter of course, since aldehyde is known to be converted into paraldehyde with very great readiness, a small quantity of metaldehyde being formed simultaneously.

They further hold that the body described by them as acetal is not paraldehyde, as Kekulé suggests. Apart from the difference in boiling point (acetal 105°, paraldehyde 125°), the composition and molecular weights of the two bodies are so different, that the numbers obtained leave no doubt as to the nature of the body under examination.

Acetal.		Experiment.	Paraldehyde.
C =	61·01	60·4	54·54
H =	11·86	11·85	9·09
Density	59	57·8	66

* Deut. Chem. Ges. Ber., iv, 787.

It has been since observed that the fresh runnings contain no acetal, whereas it is present in those which have been kept some months, so that there is no doubt that alcohol and aldehyde combine directly at the ordinary temperature to form acetal.

Kekulé's hypothesis that the aldehyde is formed during fermentation by the oxidising action of the nitrates, is scarcely possible in the case of the runnings examined by the authors, which were from potatoe spirit, since the amount of nitrates in potatoes is far too small to yield so considerable a quantity of aldehyde. Further, a considerable heating of the carbon cylinders is observed on passing the spirit through them, a proof of chemical action.

Being in possession of some quantity of metaldehyde, they have made it the subject of some experiments. It corresponds, as is known, to the only known aldehyde in the methyl series; like this it is solid at the ordinary temperature, and monomolecular in the gaseous condition. Ammonia, however, has no action on it; with methaldehyde it yields the body, $C_6H_{12}N_4$. The authors are of the opinion that both compounds are hexmolecular at the ordinary temperature. They are engaged with experiments in this direction.

H. E. A.

Sulphethers of Ethylene. By F. Ewerlof.*

The following bodies were obtained by the action of ethylene bromide on sodium mercaptide:—

$C_2H_4\left\{\begin{matrix}SCH_3\\SCH_3\end{matrix}\right.$, b.p. 183°; probably converted by fuming nitric acid into methylethylene sulphin-nitrate.

$C_2H_4\left\{\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}\right.$, b.p. 210°—213°; oxidised by nitric acid to

$C_2H_4\left\{\begin{matrix}SOC_2H_5\\SOC_2H_5\end{matrix}\right.$, which forms glistening, crystalline scales, melting at 170°.

$C_2H_4\left\{\begin{matrix}SC_5H_{11}\\SC_5H_{11}\end{matrix}\right.$, b.p. 245°—255°, formed in like manner, is converted by oxidation into

$C_2H_4\left\{\begin{matrix}SOC_5H_{11}\\SOC_5H_{11}\end{matrix}\right.$, which is obtained in thin plates, melting at 145°—150°.

$C_2H_4\left\{\begin{matrix}SC_6H_5\\SC_6H_5\end{matrix}\right.$, white needles, insoluble in water, melting at 65°. It yields on oxidation with chromic acid, $C_2H_4\left\{\begin{matrix}SOC_6H_5\\SOC_6H_5\end{matrix}\right.$.

By the action of bromine, the compound, $C_2H_4\left\{\begin{matrix}SBr_2C_6H_5\\SBr_2C_6H_5\end{matrix}\right.$ is probably formed.

* Deut. Chem. Ges. Ber., iv, 716.

Sulphetheric derivatives of acetic acid :—

$\left\{\begin{matrix} CH_2SCH_3 \\ COOH \end{matrix}\right. - \left\{\begin{matrix} CH_2SC_6H_5 \\ COOH \end{matrix}\right.$, etc., have also been obtained, and are under examination in Professor Blomstrand's laboratory.

H. E. A.

On the Action of Chlorine on various bodies of the Three-Carbon Series, and on the Isomerides of Trichlorhydrin. By C. FRIEDEL and R. D. SILVA.*

THE identity of the compounds C_3H_3Cl, derived from methylchloracetol and from chloride of propylene (which had been asserted by one of the authors), having been called in question by Berthelot, they have examined the action of chlorine on propylene chloride derived from acetone, and also from iodide of allyl.

When chlorine is allowed to act in the dark on chloropropylene (prepared from acetone) cooled by ice, hydrochloric acid is evolved during the whole of the reaction. If the process be stopped after a while, the liquid distilled, the portion distilling below 60° again submitted to the action of chlorine, and the liquid fractionally distilled, dichloropropylene, $C_3H_4Cl_2$ is obtained, boiling at 93°. By the action of bromine in diffuse daylight, a chlorobromide is formed, $C_3H_4Cl_2Br_2$, which boils from 200°—205°. Dichloropropylene, heated with alcoholic potash to 100°, yields a chlorinated ether by the substitution of $(OC_2H_5)'$ for Cl.

Chloropropylene from acetone, subjected to the action of chlorine in sunlight or bright diffused light, and cooled by ice, yields an isomeride of trichlorhydrin boiling between 122° and 126°.

Chloropropylene prepared from iodide of allyl, boils at the same temperature as that from acetone (25° to 28°), yields a dichloropropylene having the same boiling point as the one already described, and with bromine a chlorobromide boiling between 200°—205°. Alcoholic potash acts in the same manner on this dichloropropylene as on the one before described. These facts the authors regard as conclusively demonstrating the identity of the two compounds, C_3H_5Cl, derived from acetone and from propylene.

A. P.

On the Action of Phosphorus Pentachloride on Dichloraldehyde. By E. PATERNÒ and G. PISATI.†

WHEN dichloraldehyde, prepared by distilling dichloracetal with strong sulphuric acid, and purified by treating it with phosphoric anhydride, distilling, and collecting the portion which passes over at 88° to 90°, is added by drops to phosphorous pentachloride in a cooled vessel

* Compt. rend., lxxiv, 955. † Gazzetta chimica Italiana, i, 461—469.

connected with an ascending condenser, and the oily product separated by water is distilled in a current of steam and then subjected to fractional distillation, a transparent liquid is obtained, boiling at 147°, together with a small quantity of another liquid boiling at 250°. The former has the composition of tetrachlorethane, $C_2H_2Cl_4$, and is formed, according to the usual reaction of phosphorus pentachloride on aldehydes, by the substitution of 2 at Cl. for 1 at. O in dichloraldehyde:—

$$\begin{matrix} CHCl_2 \\ COH \end{matrix} + PCl_5 = PCl_3P + \begin{matrix} CHCl_2 \\ CHCl_2. \end{matrix}$$

The compound $C_2H_2Cl_4$ thus obtained is a transparent, colourless, strongly refracting liquid, insoluble in water, miscible with alcohol and ether, smelling like chloroform, and tasting sweet at first, afterwards burning and disagreeable. It boils at 147° (corr.), and has a density of 1·614 at 0°, 1·578 at 24·3°, 1·522 at 100·1°. It is identical with the compound which Berthelot and Jungfleisch* obtained by direct addition of chlorine to acetylene, having the same boiling point, and likewise yielding with potash a compound, C_2HCl_3, boiling at 87° to 88°. Both modes of formation of the compound $C_2H_2Cl_4$ show that it is symmetrical in structure, as represented by the formula $\begin{matrix} CHCl_2 \\ CHCl_2 \end{matrix}$. The same structure belongs in all probability to Regnault's chloride of dichlorethylene and to Geuther's trichlorinated ethyl chloride.

When the compound C_2HCl_3, resulting from the action of potash on tetrachlorethane, is subjected to the action of antimony pentachloride, it takes up 2 atoms of chlorine, and is converted into pentachlorethane, C_2HCl_5, boiling at 158°. The same compound is obtained by the action of phosphorus pentachloride on chloral, and is in all probability identical with the tetrachlorinated ethyl chloride and trichlorethylene chloride which Regnault obtained by the action of chlorine in sunshine on ethyl chloride and ethylene chloride respectively.

Paternò had found† that when crude dichloraldehyde, prepared as above, but contaminated with hydrochloric acid, sulphurous acid, and water, is subjected to the action of phosphorus pentachloride, the chief product is a body, $C_4H_4Cl_6O$, containing the elements of tetrachlorethane and dichloraldehyde. To determine which of the above-mentioned impurities gives rise to this difference in the result, the authors examined the action of the pentachloride on dichloraldehyde—(1) saturated with hydrochloric acid; (2) saturated with sulphurous acid; (3) mixed with $\frac{1}{2}$ mol. water. The first yielded chiefly $C_4H_4Cl_6O$, with a small

* Compt. rend., lxix, 542.

† Giornale di Scienze naturali ed economiche, v, 123.

quantity of $C_2H_2Cl_4$, the second and third chiefly $C_2H_2Cl_4$, the total product, however, being smaller in the third case. The authors leave it for the present undecided whether the compound $C_4H_4Cl_6O$ consists of hexchlorinated ethyl oxide, $C_2H_2Cl_3-O-C_2H_2Cl_3$, or of a true condensation-product having all its carbon-atoms in a single chain.

H. W.

Action of Sunlight on Olive Oil. By LUIGI MOSCHINI.*

OLIVE oil in its natural state contains in solution a yellowish substance, which, when the oil is treated with acids or with caustic soda, gives rise to the well known greenish coloration. By exposure to sunshine this colouring matter is essentially altered, the oil being thereby decolorised and no longer exhibiting a greenish colour when treated with the reagents above mentioned. Moreover, other changes take place at the same time in the constituents of the oil, the olein in particular being greatly altered, and acquiring the fundamental property of *elaïdin*, namely, that of not solidifying in contact with nitrate of mercury mixed with nitrous products. At the same time free acids are formed, and the oil acquires a rancid taste and odour.

From these results it appears that the method, suggested by some authors, of distinguishing olive-oil from other oils by means of sulphuric acid, caustic soda, and nitrate of mercury, can be depended upon only when the oil is in its natural state, not altered by exposure to sunshine.

H. W.

On the Elementary Composition of Vegetable Fats, and the Amount of Digestible Fat in Fodder. By J. KÖNIG.†

THE fat was extracted by ether after the plan followed by Stohmann. The amount yielded by various vegetable substances is given below. In the case of drying-oils, both the seed and ethereal extract were dried in a stream of hydrogen; neglect of this precaution gives a result above the truth. The ethereal extracts were freed from chlorophyll by means of animal charcoal, except in the case of the oil-seeds. This treatment involves a slight loss, as the charcoal obstinately retains a little fat.

* Gazzetta chimica Italiana, i, 580.

† Versuchs-Stationen Organ., xiii, 241—255.

	Fat per cent. in fresh substance.	Fat per cent. in dry substance.		Fat per cent. in fresh substance.	Fat per cent. in dry substance.
Linseed	31·94	35·21	Rye	1·35	1·44
Rape seed	41·90	45·49	Wheat	1·14	1·23
Hemp seed	32·37	35·25	Oats	4·04	4·53
Poppy seed	40·07	43·39	Barley	1·51	1·59
Beech-nut	23·08	28·18	Maize	4·47	4·85
Palm-nut kernel	48·07	52·85	Lupin	5·20	6·10
Earth-nut	51·51	55·25	Peas	·81	·93
White sesame ..	49·31	52·50	Beans	·83	·96
Black sesame ..	46·02	49·28	Grass hay	1·39	1·52
Cocoa-nut	64·48	67·76	Clover hay	1·43	1·61
Madia seed	37·32	40·44	Rye straw	·76	·83
Cotton seed	19·49	21·72	Oat straw	·81	·88

The fat obtained from the purified ethereal extract is, in the case of hay, a mixture of fat and wax. These may be separated with tolerable accuracy by dissolving the crude fat in hot absolute alcohol, the wax then separating on cooling; it is washed with cold alcohol, and weighed. Among the seeds examined, rye alone contained an appreciable amount of wax. Dry fodder gave the following percentages of fat and wax:—

	Fat.	Wax.		Fat.	Wax.
Meadow hay (mean of five samples) ..	1·07	·45	Rye straw	·52	·31
			Oat straw	·55	·33
			Rye grain	1·35	·09
Clover hay	1·23	·38			

The elementary composition of the various fats was determined from fats purified by treating their ethereal solution with animal charcoal. The lupin fat was further treated with hydrochloric acid, and again exhausted with ether, to separate the alkaloid which it contains. In the following table the fluid or solid nature of the fat is indicated by the letters *f* and *s*.

Consistence of fat.	Source of fat.	C.	H.	O.
f	Linseed	77·40	11·10	11·50
,,	Poppy seed	76·57	11·41	12·02
,,	Hemp seed	76·00	11·30	12·70
,,	Rape seed	78·04	12·04	9·92
,,	Beech-nut	76·65	11·47	11·88
,,	Madia seed	77·23	11·41	11·36
,,	White sesame	77·38	11·59	11·03
,,	Black sesame	76·17	11·44	12·39
,,	Cotton seed	76·40	11·53	12·27
s	Earth-nut	75·73	11·57	12·70
,,	Palm-nut kernel :—	..	..	..
f	*a*, sol. in cold alcohol	73·03	11·64	15·33
s	*b*, little soluble in cold alcohol	75·23	11·83	12·94
	Portion soluble in cold alcohol :—			
f	Meadow hay	76·43	11·17	12·40
,,	Clover hay	77·14	12·78	10·08
s	Rye straw	77·39	12·30	10·31
,,	Oat straw	78·60	12·39	9·01
,,	Pea straw	79·29	12·77	7·94

Consistence of fat.	Source of fat.	C.	H.	O.
s	Cocoa-nut	74·16	11·72	14·12
f	Rye	76·71	11·79	11·50
,,	Wheat	77·19	11·97	10·84
fs	Barley	76·29	11·77	11·94
f	Oats	75·67	11·77	12·56
,,	Maize	75·79	11·43	12·78
,,	Lupin	75·94	11·59	12·47
,,	Peas	76·71	11·96	11·33
,,	Beans	77·50	11·81	10·69
s	Potatoes	76·17	11·85	11·98
,,	Mangolds	76·12	11·69	12·19
f	Rice meal	76·17	11·51	12·32
	Portion scarcely soluble in cold alcohol :—			
s	Meadow hay	81·70	13·70	4·60
,,	Clover hay	82·50	13·26	4·21
,,	Rye straw	80·17	12·46	7·37
,,	Oat straw	83·54	13·85	2·61
,,	Pea straw	83·51	14·24	2·25

The percentage composition of the various fats agrees in most cases with that of a mixture of the three glycerides:—

Triolein	77·38 carbon.	11·76 hydrogen.	10·86 oxygen.
Tristearin	76·85 ,,	12·36 ,,	10·79 ,,
Tripalmitin	75·93 ,,	12·16 ,,	11·91 ,,

Rape oil gives an unusually high proportion of carbon; this arises from its containing the glyceride of brassic acid. Earth-nut fat apparently contains fatty acids low in the series, as the fats known to be present, namely, palmitin, arachin, and hypogæin, have all more carbon than was found on analysis. Palm-nut kernel fat is probably rich in some of the lower fatty acids; its odour is particularly suggestive of such a circumstance. Cocoa-nut fat is known to contain the glycerides of rutic, caprylic, and caproic acids; the presence of these accounts for the low carbon found. The specimens of oat, maize, and lupin oil had become somewhat oxidized by exposure to air. The oil of maize is apparently a drying oil.

The author and Dr. Dietrich made experiments on the digestibility of the fat of meadow and clover hay. They conclude that the true fat alone is digested, and that the whole of the wax is found in the excrement. The quantity of fat in the fodder soluble in cold alcohol, represented in fact the quantity digested by the animal. The digestible

fat of dry hay is 1 to 1·3 per cent.; that of rye and oat straw ·4 to ·6 per cent. The fat of pea straw is wholly wax.

The composition of the wax found in the excrement was as follows:—

	Portion soluble in cold alcohol.			Portion scarcely soluble in cold alcohol.		
	C.	H.	O.	C.	H.	O.
Meadow hay	80·51	12·41	7·08	83·25	14·38	2·37
Clover hay	79·53	12·43	8·04	82·74	13·65	3·61

From these analyses the author concludes that hay contains at least two kinds of wax, the one containing the least carbon being the most soluble in alcohol. He suggests that a hydrocarbon may possibly be present, as the percentage of carbon and hydrogen in the portion insoluble in alcohol is higher than in any known member of the fatty series.

R. W.

Note on Artificial Alizarin. By B. Boettger and Th. Petersen.*

As Liebermann has expressed some doubts as to whether the diamidanthraquinone and its derivatives, which were previously described, yield alizarin when fused with caustic potash, the authors have repeated their experiments and found their former observation completely confirmed. The alizarin obtained was analysed, and its spectrum compared with artificial and with natural alizarin. No difference could be observed in these spectra.

C. S.

Dissociation-tensions of Ammonium Carbamate. By A. Naumann.†

On volatilizing ammonium carbamate it is completely decomposed into ammonia and carbon-dioxide. Five determinations of the vapour-density, made with Hofmann's apparatus at temperatures ranging between 37° and 100°, gave numbers between 0·896—0·891, the density calculated for $2NH_3+CO_2$ being 0·898. The apparatus has to be heated for one hour before the volume becomes constant, and at low temperatures the tension reaches its point of saturation with extreme slowness, increasing very gradually when previously below this point,

* Deut. Chem. Ges. Ber., iv, 778—779.

† Deut. Chem. Ges. Ber., iv, 779—783; fully Ann. Ch. Pharm., clx, v, 29.

and decreasing as slowly as the temperature is lowered. Bodies which volatilize without decomposition, as naphthalene and carbon sesquichloride, behave differently.

From a great number of experiments the following table was calculated:—

Dissociation-Tensions of Ammonium Carbonate.

Temp.	Tension.	Temp.	Tension.	Temp.	Tension.	Temp.	Tension.
−15°	2·6 mm.	10°	29·8 mm.	26°	97·5 mm.	42°	278 mm.
−10°	4·8	12°	34	28°	110	44°	316
− 5°	7·5	14°	39	30°	124	46°	354
0°	12·4	16°	46·5	32°	143	48°	402
2°	15·7	18°	53·7	34°	166	50°	470
4°	19	20°	62·4	36°	191	55°	600
6°	22	22°	72	38°	219	60°	770
8°	25·7	24°	84·8	40°	248		

This table shows that the dissociation-tension of ammonium carbamate increases by increase of temperature similarly to the tensions of other substances. C. S.

On the Behaviour of some Diazo-compounds with Alkaline Bisulphites. By A. Strecker.*

Diazobenzene nitrate is readily soluble in a solution of potassium bisulphite, the liquid becoming hot, and sulphur dioxide is given off. On cooling it solidifies to a magma of yellow crystals, which by recrystallisation from boiling water are obtained in the form of colourless, shining scales, having the composition $C_6H_7N_2SO_3K + H_2O$. It does not explode on heating, and yields neither ammonia nor aniline when heated with soda lime. When it is heated with nitric acid, sulphuric acid is formed. On adding barium chloride to the hot solution, the salt, $(C_6H_7N_2SO_3)_2Ba$, containing water of crystallisation, separates on cooling in colourless crystals. When silver nitrate is added to the solution of the potassium salt, metallic silver is precipitated as a white powder, and the yellow solution yields on evaporation fine yellow shining plates of a silver salt, which explodes when gently heated; the composition of this salt has not been ascertained.

By acting with potassium bisulphite on diazobenzene-sulphonic acid, the compound $C_6H_8N_2SO_3$ is formed, according to the equation—

$$C_6H_4N_2SO_3 + 2HKSO_3 + 2H_2O = C_6H_8N_2SO_3 + H_2SO_4 + K_2SO_4.$$

This acid crystallises from boiling water in colourless shining needles or plates. By boiling it with nitric acid no sulphuric acid is formed,

* Deut. Chem. Ges. Ber., iv, 784—787.

and when it is heated with soda lime, only half of the nitrogen is given off as aniline (or ammonia).

The barium salt, $(C_6H_7N_2SO_3)_2Ba+5H_2O$, obtained by boiling the solution with barium carbonate, crystallises in long lance-shaped light yellow needles. The lead salt $(C_6H_7N_2SO_3)_2Pb+2H_2O$ forms small white crystals. The acid reduces silver and mercury salts; its salts are isomeric with those obtained from diazobenzene nitrate.

C. S.

Methyldiphenylamine. By C. BARDY.*

IN a paper inserted in the Compt. rend. of the 4th September last, Girard and Vogt announce the discovery of methyldiphenylamine, obtained by the action of methylaniline on aniline hydrochloride, although the method of preparation and the reactions of this base had been described by the author in January, 1870, and reproduced the same year in a scientific journal.†

When diphenylamine is heated with methyl iodide, or when the hydrochlorate is acted upon under pressure by methylic alcohol, according to Berthelot's method, a colourless liquid is obtained, boiling at 290°, and having an agreeable odour recalling that of diphenylamine. It gives a magnificent violet coloration with nitric acid, and a fine blue by the action of reducing agents. It is evident from the method of its formation that this is the true methyldiphenylamine. On the contrary, the volatile liquid obtained by Girard and Vogt by the action of methylaniline on aniline hydrochloride, has nothing in common with this base, except the boiling point, neither does it contain any of it, as the least trace would be revealed by the action of nitric acid, producing the characteristic blue colour. The author concludes, therefore, that the base obtained by Girard and Vogt is only an isomeride of the true methyldiphenylamine.

C. E. G.

Allantoïn and Bodies Derived Therefrom. By E. MULDER.‡

Preparation.—In working by Liebig and Wöhler's method, the author found the yield increased when more water than usually recommended was taken, viz., about one litre for every 25 grams of uric acid. The greatest yield, however, was obtained by effecting the decomposition at the ordinary temperature; 100 grams uric acid were stirred up in 1 to 2 litres of water, a small quantity of acetic acid added, and the necessary quantity of plumbic peroxide then gradually introduced. The beaker containing the mixture was exposed to bright daylight.

* Compt. rend., lxxii, 751—752.

† Brevet, No. 88,713; Moniteur Scientifique, 1870, 553.

‡ Ann. Ch. Pharm., clix, 349—365.

The acetic acid is added in order to start the decomposition, which is promoted by light. For 100 grams uric acid the peroxide from 1·5 kilogram red lead was required; both the peroxide and the uric acid were employed in the dried state. The decomposition being ended, the whole is heated, filtered, and the residue repeatedly exhausted with warm water; the filtrates, to which a small quantity of acetic acid is added, are evaporated and filtered. On cooling the allantoïn separates out, and a further quantity is obtained on concentrating the mother-liquor. 100 grams of uric acid thus treated yield 30—32 grams of pure allantoïn.

The formation of allantoïn is usually expressed by the equation:—

$$C_5H_4N_4O_3 + H_2O + O = C_4H_6N_4O_3 + CO_2.$$

according to which 100 grams of uric acid should yield 92 grams of allantoïn, and the loss is supposed to be due to further partial oxidation by the peroxide. The author finds, however, that allantoïn is *not* perceptibly decomposed by plumbic peroxide at the ordinary temperature, and only with extreme difficulty on heating. He believes that the formation of dialuric acid* precedes that of allantoïn, probably according to the equations:—

$$\alpha.\ 2C_5H_4N_4O_3 + 4H_2O = \underset{\text{Dialuric acid.}}{2C_4H_4N_2O_4} + \underset{\text{Urea.}}{2CH_4N_2O}.$$

$$\beta.\ 2C_4H_4N_2O_4 + H_2O + 2O = C_4H_6N_4O_3 + 2C_2H_2O_4.$$

In this case 100 grams uric acid should yield 46 grams allantoïn.

Allantoïn Nitrate.—A mixture of 2 grams allantoïn and 3 grams ordinary nitric acid was allowed to stand for some weeks over lime. The apparently amorphous product was analysed and gave numbers agreeing with the formula, $C_4H_6N_4O_3,HNO_3$. It is decomposed by water allantoïn crystallising out; also by alcohol, which leaves a residue of allantoïn. Allantoïn combines with sulphuric acid, but the compound was not analysed.

Allanic Acid.—Allantoïn is readily dissolved by nitric acid (1·35 sp. gr.) on warming on the water-bath. After evaporating a sticky mass remains, which becomes hard, transparent, and amorphous on cooling. This, recrystallised several times from water, gave beautiful starlike groups of needles, which contain 1 molecule of water of crystallisation. Dried at 110°, their composition is $C_4H_5N_5O_5$. This body has an acid reaction; it is difficultly soluble in cold water; on evaporation of its aqueous solution it is gradually decomposed. Ammonia dissolves it readily at ordinary temperatures, the solution depositing on standing

* Gibbs has shown that allantoïn may be obtained by the oxidising action of nitrous acid on dialuric acid.

well formed prisms of a salt having the composition, $C_4H_5N_5O_5NH_3$. On the addition of hydrochloric acid to a concentrated solution of this salt, the free acid crystallises out in concentric groups of needles as before. Silver nitrate in ammoniacal solution produces an amorphous precipitate, which, after re-crystallisation from water, has the composition $C_4H_4AgN_5O_5$ + aq. Allanic acid decomposes at 210—220°, without previously melting. It is precipitated by neutral lead acetate, but not by the basic acetate; the precipitate suspended in water and decomposed by hydrogen sulphide, yields on evaporation at ordinary temperatures, well crystallised allanic acid. By the above method but little acid is formed; a better yield is obtained by gradually adding nitric acid containing much nitric peroxide to finely powdered allantoïn contained in a well cooled porcelain dish, until the whole is dissolved. On allowing the solution to stand for some time, a crystalline crust formed, which when re-crystallised from water, gave the characteristic needles of allanic acid. The yield is about 50 per cent. of the allantoïn employed. Three lead-salts of the acid were obtained, one normal and two basic: $C_4H_4PbN_5O_5$ + aq.: $C_4H_4PbN_5O_5.2PbHO$; $C_4H_4PbN_5O_5.3PbHO$. Other salts were also prepared, viz., silver, barium, potassium, magnesium, but not analysed. That allanic acid is not nitroallantoïn, $C_4H_5(NO_2)N_4O_3$, seems probable to the author from the fact that even its silver salt is not explosive; that it is not reduced by hydrogen sulphide in strongly ammoniacal solution; that it is less easily reduced than allantoïn by concentrated hydriodic acid.

Allanturic Acid.—On allowing the mother-liquor from the preparation of allanic acid by the first of the above methods to stand in an exsiccator, a further quantity of the acid crystallised out, accompanied by an evolution of gas; well formed prisms of urea nitrate were obtained at the same time. The syrupy residue was freed from crystals by washing with a little cold water, allowed to stand, and this operation repeated until no further deposition of crystals or evolution of gas took place. The solution was then fractionally precipitated by basic lead acetate. Analysis of one of the later precipitates gave carbon, 10·6 per cent.; nitrogen, 10·9 per cent.; lead, 57·1 per cent. The acid of this lead salt is probably identical with Pelouze's allanturic acid, to which he assigned the formula $C_{10}H_{14}N_5O_9$; his analysis, however, gave less nitrogen than is required by this formula. The author considers allanturic acid to be identical with the acid of his lead-salt, and that its formula is, $C_7H_{10}N_6O_6$. This contains the same percentage quantities of carbon and nitrogen ($12 \times 7 = 14 \times 6$), with which the results of the above analysis agree. Its formation may be expressed by the equation:—

$$2C_4H_6N_4O_3 + H_2O = CON_2H_4 + C_7H_{10}N_6O_6.$$

Allantoïn was also similarly decomposed by evaporation with hydrochloric acid. The lead salt of the resulting acid gave carbon, 10·8 per cent.; nitrogen, 10·8 per cent. Allanic acid was not noticed among the products of the decomposition of allantoïn by hydrochloric acid. But very small quantities of allanturic acid were obtained by either of the above methods.

Preparation of Allantoïn by Schlieper's Method.—This consists, as is known, in the employment of potassium ferricyanide as oxidiser, the uric acid being dissolved in potassium hydrate solution. The yield is about the same as when the peroxide is employed, and the quantity of salt used is in accordance with the equation before given for the formation of allantoïn. The formation of the red body, from which Schlieper could only purify his allantoïn with difficulty, was readily avoided by using less water than he directs, and by neutralising with acetic acid.

Potassium Allantoïn.—Obtained by adding potassium hydrate to finely powdered allantoïn, suspended in water until complete solution is effected. The solution mixed with alcohol and allowed to stand over lime, deposits the salt, which, after re-crystallisation from aqueous alcohol, forms a beautiful silky, glistening, voluminous mass of the composition, $C_4H_5KN_4O_3$. It is extremely soluble in water, and has an alkaline reaction; on the addition of acetic acid, allantoïn separates out after some time.

Allantoic Acid.—Acetic acid causes no precipitate in a solution of allantoïn in an excess of aqueous potassic hydrate which has stood some days. Acetic acid was added to acid reaction, also a little alcohol, and the whole allowed to stand over lime. A body then separates out in the form of a hard crust, which after recrystallisation, has a neutral reaction. Its composition is represented by the formula, $C_4H_7N_4KO_4$. The mother-liquor contains neither urea nor oxalic acid, and about a theoretical yield of the salt is eventually obtained. The formation of an acid by the action of potassium hydrate was noticed by Schlieper; he analysed an amorphous lead salt of what he termed hydantoic acid, $C_4H_8N_4O_4$. His salt was probably impure, as the above salt gives a crystalline precipitate with lead acetate.

Lantanuric Acid.—Schlieper obtained the acid potassium salt of an acid of the composition, $C_3H_4N_2O_3$, by the action of potassium hydrate on the impure allantoïn prepared by the action of potassium ferricyanide on uric acid. The author could not obtain the same product with pure allantoïn. Possibly Schlieper's acid is an oxidation product of allantoïn, due to the employment of an excess of ferricyanide.

H. E. A.

Melolonthine, a New Crystalline Substance from the Animal Body. By PHILIP SCHREINER.*

THE substance described under the name of melolonthine was extracted, together with leucine and other matters, from the body of the common cockchafer (*Melolontha vulgaris*), by freeing the watery decoction of the insects from albumin and other substances by boiling and treatment with lead acetate. On removing the excess of lead by hydric sulphide, and concentrating, a crop of crystals was obtained, which, when exhausted by alcohol, left melolonthine as a residue. The substance was obtained pure by recrystallisation from very dilute solution of ammonia. 30 pounds of the insects furnished 1·5 grams of melolonthine.

Melolonthine is a beautiful, silky, lustrous, crystalline body, tasteless and odourless. It is soluble with difficulty in cold, but more readily in hot water; quite insoluble in alcohol and ether. The caustic and carbonated alkalies dissolve it readily. The aqueous solution has no action on vegetable colours.

The author assigns to melolonthine the formula, $C_5H_{12}N_2SO_3$. This formula differs from that of cystine by the elements of a molecule of acetamide, and from taurine by the elements of a molecule of proprionitrile.

T. S.

On Chlorophyll and some of its Derivatives. By E. GERLAND and N. W. P. RAUWENHOFF.†

THE authors have examined the absorption-spectra of freshly prepared chlorophyll, of an alcoholic solution of chlorophyll which had been kept for several years in the dark, and of some of the derivatives of chlorophyll. These absorption-spectra are laid down in a series of diagrams, according to the method of J. Müller.

A freshly prepared alcoholic solution of chlorophyll, from *Brassica oleracea* var. *crispa*, gives five absorption-bands, of which the first, in the red, is divided into two by a somewhat lighter central interval. An alcoholic solution of chlorophyll which had been prepared in 1865 from *Tilia europea*, gave the spectrum of modified chlorophyll, the solution not having suffered any further decomposition in the course of 5½ years. The spectrum of modified chlorophyll shows the first band also divided into two. On evaporating a solution of chlorophyll in weak spirit on a sand-bath, all the chlorophyll was precipitated, and, on examination, proved to be modified chlorophyll; the supernatant liquid contained aldehyde. This seems to show that the opinion of Timiriaseff, according to which modified chlorophyll is formed by reduction, is correct.

* Deut. Chem. Ges. Ber., iv, 763—765. † Pogg. Ann., cxliii, 231—238.

Films of solid chlorophyll, as well as green leaves, show the same absorption-bands as a freshly prepared alcoholic solution of chlorophyll. The authors finally, as Filhol and Timiriaseff had done previously, arrive at the conclusion that chlorophyll is composed of a yellow and a green colouring matter, which may be separated from each other by simple filtration through animal charcoal. These two colouring matters are not, however, the phylloxanthin and phyllocyanin of Frémy; the former of these seems to be nothing but modified chlorophyll. Nor are they the yellow and green colouring matters prepared from chlorophyll by Kromeyer. Neither of these two pairs of substances is capable of forming chlorophyll.

In leaves that become yellow it appears that the chlorophyll disappears either by being absorbed, or by becoming converted into the yellow component.

A. D.

Physiological Chemistry.

Influence of Quinine on Oxidation in the Blood. By ADAM SCHULTE.*

QUININE has been found by Binz to have an extraordinary power of arresting the processes of fermentation and putrefaction, and to be a powerful poison for low organisms, or, to speak more generally, for all moving bodies consisting of protoplasm. It kills the fungi and bacteria, etc., which accompany fermentation and putrefaction, and puts a stop to these processes themselves. It arrests the motions of the white blood-corpuscles, and thus prevents them from making their exit from the blood-vessels. It therefore diminishes or arrests the formation of pus in inflammation, pus consisting in great measure, according to Cohnheim's well known theory, of an accumulation of white corpuscles which have issued from the vessels. It destroys the power of certain substances to produce ozone. The red blood-corpuscles have this power, and by depriving them of it, quinine, when present in the blood, must diminish tissue-change in the body, and thereby lessen the production of heat. That it does diminish the temperature of the body, and therefore proves useful in fever, has been demonstrated by direct observation, and its power to lessen tissue-change has been shown by the observations of Ranke and Kerner, who found that the amount of uric acid and urea excreted daily in the urine became much less when large doses of quinine were taken. Simple examination of the urine, however, although it may show that the tissue-change is

* N. Repert. Pharm., xx, 539—565.

diminished, yields no information regarding the extent to which this is due to the direct action of quinine on oxidation, and how much to its indirect influence through the nervous system. The only previous observation on this subject is one of Harley, who found that blood to which quinine had been added in the proportion of 1 part to 12,000, took up less oxygen, and gave off less carbonic acid than normal blood.

The changes in the alkalinity of the blood observed by Zuntz, furnish a much more convenient method of investigating oxidation in it than the gas analysis used by Harley, and this method was employed by Schulte in his experiments. Zuntz noticed that a considerable formation of acid began to take place in blood immediately after it was drawn, and continued in a less degree until putrefaction commenced. As the formation was most abundant in the first few minutes before coagulation took place, he thought it a vital phenomenon. The amount of acid formed was estimated by the diminution it produced in the alkalinity of the blood. The process employed for this purpose depends on the fact that the colouring matter of blood-corpuscles does not diffuse out of them into sufficiently concentrated solutions of sodium chloride, while the alkalies or salts they contain do so readily. The alkalinity was determined by means of dilute phosphoric acid, to which a quantity of sodium chloride had been added, sufficient to prevent the blood-corpuscles from being dissolved, and the reaction interfered with by their colouring matter. The point of saturation was held to be reached whenever a distinct reddening of blue litmus paper was produced, even although the red disappeared immediately. This transient reddening by carbonic acid was chosen rather than the first permanent reddening, because it could be more easily observed. The absolute amount of alkalinity is not ascertained thus, but the comparative amount of different samples of blood is all that is wanted, and if they be treated alike as regards temperature, shaking, &c., the error caused by the carbonic acid is the same in all. The amount of error may be approximately estimated by noting the point at which a transient reddening occurs in the cold, in a solution of sodium carbonate of nearly the same alkalinity as the blood, and then determining the real alkalinity of the boiling solution. The litmus paper used should be made of smooth satin paper, and must not be too deeply tinted. The tincture with which it is prepared should have acid added to it in quantity sufficient to give it a violet tint. When used it should be moistened with solution of sodium chloride, a drop of blood placed upon it for a few seconds, and then removed by blotting-paper, with the aid of a drop of solution of sodium chloride.

By means of this method, Zuntz and Scharrenbroich found that quinine and berberine lessen the production of acid, and Schulte, by the experiments which he here details, confirms this result; shows that

quinine can stop it both before and after the coagulation of the blood, that sodium nitropicrate has a similar action to quinine, and is nearly as powerful, while cinchonine has a very much smaller effect. Harley found that while quinine lessened oxidation in blood, other substances, such as snake-poison, increased it. It would seem from the experiments of Binz that similar processes occur in the living body, for when putrid fluids were injected into the circulation of an animal, its temperature rose, but if they were previously mixed with quinine, or if a dose of quinine were injected along with it, the rise of temperature was arrested or much diminished. The author gives the results of some researches communicated to him by Zuntz, on the influence of quinine on the tissue-change and the excretion of urea. The experimenter put himself on a constant diet, and after the daily amount of urea excreted had become constant, he took three doses of 0·6 grm. of hydrochlorate of quinine for two days. The amount of urine at first increased by a third, and then sunk as much. The specific gravity sank from 1,018 to 1,012; the urea sank one-third on the first day on which quinine was taken, and became still further diminished on the second. As soon as the quinine was stopped, the urea increased, and on the fifth day again reached its normal amount. Quinine could be detected in the urine by the iodine test till the third day. The diminution of urea is large, compared with that found by Kerner, but during the present series of experiments no tea or coffee were taken, and these would lessen the urea on the days when no quinine was taken in his observations. Unruh has found similar but less distinct results in cases of fever, but it is doubtful whether the quinine he administered was all absorbed.

T. L. B.

On a Blue Colouring Matter in the Bile. By E. Ritter.*

Städeler and Jaffé have shown that a blue colouring matter can be obtained by the action of nitric acid on the biliary pigments. Ritter describes a blue colouring matter, which he regards as a constituent of the bile, and not as a product of chemical action. He finds it in the bile of man, the ox, the sheep, the pig, the dog, and the cat. It is prepared as follows:—

Bile is shaken with chloroform, till a yellow solution is obtained, and the yellow chloroform solution is treated with soda, till the colour entirely disappears. On neutralisation with hydrochloric acid, two layers are formed, one of which contains the yellow chloroform solution, the other the blue colouring matter in a state of suspension. The colouring matter is insoluble in chloroform and acids. It dissolves in alkalies, forming a colourless or yellowish solution. When this

* N. Repert. Pharm., xx, 569.

solution is neutralised with acids and exposed to the air, a brown precipitate forms, which after a few days, but sometimes only after a month, again becomes blue. Reduced indigo, on the other hand, dissolved in alkalies, becomes instantaneously blue on exposure to the air.

D. F.

On the Nutritive and Assimilative Processes in Fungi. By Ph. Zöller.*

Dr. Zöller has made experiments with a view to throw light on the process of formation of the higher from the more simple carbonaceous assimilation products of the vegetable world. In order that the process of assimilation might be studied independent of the action of chlorophyll and light, the spores of mould were chosen as representatives of the chlorophyll-free vegetable cell. As there were no direct experiments proving the formation of carbohydrates and more highly organised products immediately from the simple elements, the author employed an organic acid—acetic—as the source of carbon in his experimental solutions.

The object of the first set of experiments recorded was to determine whether the spores would grow in a solution containing the ashes of plants, acetic acid, and ammonia. The solution prepared with freshly distilled water contained ammonium acetate, potassium acetate, sodium acetate, calcium acetate, magnesium acetate, potassium superphosphate, and calcium sulphate, in the proportion of 1·5 p. c., or 15 grammes per litre. This solution was placed in flasks in the proportion of two litres to each. Each flask was closed with a cork, through which passed two tubes, one of which ended immediately below the cork, while the other reached down to near the surface of the liquid. The free arms were connected with tubes filled with cotton wool and caustic potash.

By this arrangement the access of carbonic acid from the air was prevented, as also the entrance of spores, while at the same time it allowed of the flask being filled with air free from carbonic acid at the commencement of the experiment. Spores sown in this liquid developed and accumulated chiefly on the surface. The development was slow, and comparatively insignificant, due in part to the composition of the liquid, especially as regards the phosphates, partly to the concentration. The experiments were conducted in the winter, between October and April, so that probably also the low temperature retarded the growth and development of the fungi. After a growth of six months, the yield of dry fungi by eight litres of the solution was only 2·316 grammes. Analysis proved that with an ash of 6·877 p. c., the

* N. Repert. Pharm., xx, 513—520.

fungi had developed from the solution a fluid fat, soluble and insoluble carbohydrates, and also albuminoids.

A second set of experiments was made, with slightly different and less concentrated solutions. Instead of potassium phosphate, sodium phosphate was used, and the concentration was only one-third that of the former solution. In this set of experiments, two solutions were employed of the following composition:—

	No. 1.	No. 2.
Ammonium phosphate	1·50	—
Sodium phosphate.....	—	1·00
Ammonium acetate	1·50	3·00
Potassium ,, ...	0·70	0·70
Sodium ,, ...	0·50	—
Calcium ,, ...	1·20	1·20
Magnesium ,, ...	0·10	0·10
Calcium sulphate	0·04	0·04
	5·54 per litre.	6·04 per litre.

The first solution was clear, and had a neutral or slightly acid reaction. The second solution was opalescent and alkaline. The solutions were placed in flasks as before, but only 1 litre was placed in each. These experiments were performed in June, 1871.

In a few days the spores sown in fluid I, which contained phosphoric acid, in the form of ammonium phosphate, had undergone considerable development, and on the 4th July had formed a thick crust; this, when dried at 100° C., weighed 1·465 grm. The reaction of the solution remained the same as before. The condition of solution II was quite different; the spores did not show any tendency to develop, nor did fresh spores sown at the end of 14 days germinate, even though the solution in the flask was freely exposed to the air. In order to determine whether the alkalinity of the solution was the cause of the non-development, the liquid was acidified with acetic acid, and fresh spores sown; even at the end of a week the development was a matter of doubt, though there were slight indications of germination. An alkaline reaction of the fluid is thus seen to lessen, or even entirely prevent the development of fungi. Even when the solution exhibited the proper reaction, it was only when the phosphoric acid was in the form of ammonium phosphate that the development was at all rapid. Both in the first set of experiments and in solution II, where the phosphoric acid was presented in the form of potassium phosphate and sodium phosphate respectively, the development was very slow and inconsiderable.

From the first set of experiments, after a growth of six months only,

2·316 grm. dry material were obtained from 8 litres (0·3 grm. per litre), while from solution I, after three weeks growth, 1·465 grm. per litre were obtained.

It thus appeared that fungi could build up the higher organic vegetable products from such materials as an organic acid and ammonia in presence of water and the ashes of plants.

With a diminution of 68 p. c. of the amount of acetic acid in solution I, a mass of vegetation had arisen, containing 4·06 p. c. nitrogen, 47·48 p. c. carbonic acid, and 5·27 p. c. ash.

D. F.

Agricultural Chemistry.

On the Germination of Oleaginous Seeds. By A. Müntz.*

The author has experimented on the germination of three kinds of seeds: those of the radish, of the colza, and of the poppy. The germinations were effected in filter paper, kept constantly wet, or in asbestos soaked in water. With the exception of the first experiment, the germinations took place in the dark. Before and after the germination, the seed was treated with boiling water, the solution evaporated, and the extract treated with absolute alcohol, or a mixture of alcohol and ether; the author has not been able to detect glycerin in the alcoholic solution. After the treatment with water, the embryo plant is dried, powdered, and exhausted with ether; the ethereal solution evaporated, and dried at 110°. It was found in all cases that the fatty matter contained in the seeds gradually diminished during the germination, thus for instance, 5 grams of radish-seed before germination contained 1·750 grams of fatty matter: after two days' germination, the same quantity contained 1·645 grams, and after four days, 0·790 grams; at this time the cotyledons had began to turn green. The quantities of oil obtained were then treated with six times their weight of alcohol, which dissolved in the first instance 10·17 parts in 100 of oil, after two days' germination, 0·893 in 100, and after four days' germination, 0·751. It will be seen from this, that the proportion of fatty acid had increased rapidly. Analyses of the fatty acids of the colza before and after germination have been made; an analyses of the fatty acids before germination gave the following numbers:—

$$C = 76·67;\ H = 11·78;\ O = 11·55 \text{ per cent.}$$

The fatty acids of the colza after ten days' germination had the composition—

$$C = 73·85;\ H = 11·31;\ O = 14·84 \text{ per cent.}$$

* Ann. Ch. Phys. [4], xxii, 472—486.

The acids from poppy-seeds showed also the same increase in the proportion of oxygen, and decrease in the amount of carbon. The author believes that during the germination the fatty matter is decomposed into fatty acids and glycerin, and that the latter disappears at the moment it is set at liberty.

A. P.

Ash Analysis of the Cabbage. By HOFMANN.*

THE author took for his investigation the winter-cabbage, *Brassica oleracea acephala.* He examined it at two stages of its development, as young plants gathered in July, and as mature plants taken in the following January. The young plants averaged 20 cm. in height, and 4·8 grams in weight. The full-grown cabbages were 40—50 cm. in height, and their average weight, after removing the lesser roots, was 236 grms. Of this weight the leaves of the cabbage contributed 188 grms., and the stalk 48 grms. Analysis showed 100 parts in a fresh state to contain:—

	Young plant.	Winter cabbage.	
		Leaves.	Stalk.
Water	85·167	20·634	22·458
Dry substance	14·833	79·366	77·542
Ash	4·257	1·820	1·456
Nitrogen	·688	3·064	1·661

The composition of the ash in 100 parts was as follows:—

	Young plant.	Winter cabbage.	
		Leaves.	Stalk.
Potash	30·959	31·728	39·415
Soda	..	2·015	3·517
Lime	17·710	14·426	12·355
Magnesia	4·099	2·845	4·887
Ferric oxide	1·565	8·108	1·347
Phosphoric acid	7·750	10·093	12·263
Sulphuric acid	8·616	6·087	9·203
Silica	1·231	1·198	·845
Chlorine	8·189	7·640	6·805
Carbonic acid	15·175	13·114	7·878
Sand and charcoal	6·420	2·692	1·325
	101·714	99·946	99·840

R. W.

* Versuchs-Stationen Organ., xiii, 255—262.

Water-Culture Experiments with Flax. By E. CAMPENHAUSEN.*

THE author finds that flax grows with great luxuriance in a well prepared saline solution, and produces an abundance of seed; it is therefore an excellent subject for water-culture experiments. The solution he employed contained in 1 litre :—

	gram.
Potassium chloride	·43506
Calcium nitrate	·47757
Magnesium sulphate	·08726
Ferric phosphate	·03300
Monopotassic phosphate	·02200

R. W.

On Lime- and Salt-Plants. By H. HOFFMANN.†

THE author continues the account of his experiments on this subject. He maintains that "lime-plants" do not exist; but that the plants characteristic of limestone districts grow there merely from the suitability of the soil-climate, as to warmth, drainage, &c., and not in consequence of any partiality for lime. Various so-called lime-plants were grown for several years in beds of artificial soil. Growth was in all cases maintained, and seed-formation took place, to a greater or less extent, even on soil very poor in lime. In some instances the calcareous soil had no advantage whatever over the sandstone bed. The limed soil had perhaps most advantage in the case of Lucerne.

Sendtner, Kerner, and other botanists have described certain other plants as "lime-hating," and assert that on a calcareous soil such plants never bear seed. Experiments showed that some of these plants, as *Herniaria glabra*, and *Rumex acetosella*, produced perfect seed on a limed bed; while others, as *Alchemilla fissa*, yielded barren blossoms only. The last-named plant produced fully developed seed on a soil nearly free from lime.

The author further experimented with various marine plants, to ascertain if a liking for salt was the cause of their preference for the sea coast. The plants were grown in pots, to some of which common salt was applied every year. *Plantago maritima*, the ash of which, according to Uloth, contains 72 per cent. of chlorides, produced perfect seeds on a soil containing no salt, but where salt was supplied the development of seed was greater. *Salicornia herbacea*, the chlorides of which are, under normal conditions, 60 per cent. of the ash, and *Glaux maritima*, grew equally well in the salted and unsalted pots. The author believes that "salt-plants" are rather plants that can endure

* Versuchs-Stationen Organ., xiii, 264–269.

† Versuchs-Stationen Organ., xiii, 269–307.

salt, than those which require it; and that the more permanent moisture of a saline soil is probably one reason of their choice.

R. W.

Analytical Chemistry.

The Decomposition of Minerals by Sodium and Potassium. By M. SCHOENN.*

ALMOST all substances insoluble in acids, such as the silicates, fluosilicates, cyanides, titanates, chromic iron, &c., are decomposed when ignited with sodium or potassium. The reduction is best effected in a small cylindrical iron crucible, about 4 centimetres in diameter, and of equal height; sufficiently thin to be capable of being brought rapidly to a red heat, when ignited in a Bunsen flame.

The fragments of sodium or potassium are arranged at the bottom of the crucible, and covered with the mineral intended to be decomposed, the latter having been previously well dried; the crucible is then covered and quickly heated to bright redness. When the action is complete, the crucible is allowed to cool, and a little water added, in the first instance drop by drop, to the fused mass. The contents are finally treated with boiling water, and the insoluble portion is filtered off. The solution contains the alkali in combination with the chlorous portion of the mineral, while the metals or their oxides remain upon the filter. The latter having been well washed, are dissolved in hydrochloric or nitric acid, and the analysis of both solutions is completed in the usual manner. When carbonates are decomposed by the method above described, the insoluble portion will, of course, contain a certain quantity of free carbon; in the case of sulphates, however, no corresponding reduction takes place; nevertheless, when the solution is examined, the whole of the sulphuric acid will be found in combination with the sodium.

The following notes relate to the author's experience:—

Oxide of Chromium and Chrome Iron.—According to the quantity of sodium employed, the chromium is either reduced to the metallic state, or partially converted into chromate.

Fluoride of calcium is not attacked by sodium. To separate *titanic acid* from its combinations (titanic iron for example), after ignition with sodium, the hydrochloric solution is neutralised with sodium carbonate, and the iron having been peroxidised with nitric acid, the solution is boiled with sodium acetate. The whole of the titanic acid is then precipitated with the iron. The calcined pre-

* J. Pharm. Chim. [4], xiv, 190—192.

cipitate is then digested with concentrated hydrochloric acid, which slowly but completely removes the iron.

Sulphide of Molybdenum is attacked by sodium, producing a brown alkaline solution, which turns green when exposed to the air. The acid solution of the deposit, which becomes blue on exposure, is decolorised, when neutralised with ammonia and brought to ebullition, and gives, on the addition of barium chloride, a white precipitate of barium molybdate.

In a similar manner, minerals containing *tungstic acid* yield an alkaline solution, which furnishes, on addition of excess of hydrochloric acid, a white or flesh-coloured precipitate, rapidly changing to lemon-yellow. The precipitate is pure tungstic acid.

J. W.

Estimation of Cream of Tartar in Wine. By P. Carles.*

The author having recently determined the percentage of cream of tartar in several varieties of wine, both by the old process of incineration, and by the improved method lately introduced by Berthelot, publishes the results of his analysis, in order to show how widely the two processes sometimes differ in results, and to urge upon chemists the necessity of rejecting the old process, and of adopting instead the more exact method of Berthelot and Fleurieu.

In this latter process, the acid tartrate of potassium is precipitated, by adding to a known volume of the wine an equal volume of a mixture of alcohol and ether. The crystalline precipitate is collected, slightly washed with alcohol, redissolved in water, and the tartaric acid estimated by a standard alkaline solution.

The following are some of the analyses above referred to. The results calculate to one litre respectively :—

	Red wine. (Bordeaux.)	White wine. A.	White wine. B.	Malaga.
Alcohol	120·0	110·0	110·0	161·0
Cream of tartar (by calcination)	2·86	1·55	1·82	3·4
Cream of tartar (Berthelot's method)	2·32	1·45	1·10	0·95
Extract	24·50	18·50	18·00	171·40

It will be noticed that in the first two wines the percentages of cream of tartar obtained by the two processes are very nearly identical, but the variation is much greater in the two latter instances, especially

* J. Pharm. Chim. [4], xiv, 188—190

with the sample of Malaga, in which the proportion of cream of tartar indicated by calcination, is actually greater than the above mixture of alcohol and water is capable of dissolving. In the opinion of the author this anomalous result may be accounted for by the natural presence in the wine of organic potassium salts, or perhaps from the addition of molasses, or some similar product rich in salts of this nature; at all events, it is obvious that the old process is liable to frequent sources of error, especially when sweet wines are examined; it is better, therefore, to reject it altogether and to conduct the analysis by direct estimation of the cream of tartar.

J. W.

Dry Process for the Estimation of Silicon in Cast Iron, Wrought Iron, and Steel. By H. Boussingault.*

The process generally adopted for the determination of silicon in iron and steel, is not sufficiently trustworthy in its results, when the proportion of silicon contained in the iron is extremely small, and when consequently the weight of silica obtained cannot possibly exceed a few milligrams. In fact, the question not unfrequently arises, whether the silica obtained really existed in the iron as silicon, or whether it was derived from the vessels or reagents employed in the operation.

It became necessary, therefore, in order to resolve definitely the questions which the author had undertaken, that some more satisfactory process for the estimation of silicon should be devised, and after many trials, the following dry method was decided upon, experience having shown that it was entirely free from those particular sources of error which in the old process are so very liable to falsify the results.

The iron, at red heat, is submitted successively to the action of two gases. 1. Atmospheric air to oxidise the iron, carbon, and silicon. 2. Dry hydrochloric acid gas to convert and volatilize the metal in the state of chloride.

The operation is effected consequently in two stages; and this is the more necessary, inasmuch as it was found that when the iron is oxidised and converted into chloride simultaneously, by passing over the heated metal a current of hydrochloric acid gas mixed with air, the chlorination of the iron takes place more rapidly than the oxidation, and the silicon in combination, passes into the state of chloride before it is oxidised, and the whole, or at least a considerable portion is in this way lost.

The analysis is conducted in the following manner:—

About one gram of the metal, in a tolerably fine state of division, is placed in a small platinum boat and carefully weighed. The whole is

* Ann. Chim. Phys. [4], xxii, 457—472.

then introduced into a muffle and heated in a furnace to the temperature usually employed in cupellation. In two or three hours the iron will be found to be completely oxidised, and to have increased about 35 or 36 per cent. in weight; this indicates the composition 4FeO, Fe_2O_3, in which 1 gram of metal would require 0·33 gram of oxygen. The boat and its contents are next placed in a porcelain tube, heated to redness, and a slow and continuous current of dry hydrochloric acid gas passed over them. The iron is thus converted into chloride, and volatilised towards the cooler portion of the tube, while the silica, not being affected by the gas, remains untouched in the platinum vessel. When the operation is judged to be complete, the latter is withdrawn, placed in a glass tube, and re-weighed; the increase in weight is due to silica.

The silica obtained in this manner is perfectly white, in an extremely fine state of division, generally preserving the form of the oxide as withdrawn from the muffle. If this silica, for example, was derived from an iron turning coiled spirally, the silica will represent this spiral; while so great is its tenuity, that it may be compared to the ash of a linen thread, which has been carefully burnt in a still atmosphere. It is obvious, therefore, that it is important to moderate the rapidity of the current of gas during the operation, lest the silica or any portion of it be mechanically carried away.

The purity of the silica is ascertained by pouring into the boat a few drops of hydrofluoric acid and a drop of sulphuric acid; on warming, the whole should volatilize. In every estimation made by the author upon malleable iron and steel, the silica disappeared entirely by this treatment: but cast-iron not unfrequently yielded a silica containing a small quantity of earthy matter, resulting probably from an admixture of scoria with the melted metal; it was certainly not due to the presence of alumina, inasmuch as aluminium is never found in cast-iron, the author having even failed to detect it in Wootz steel, notwithstanding that Faraday's analyses tended in the opposite direction.

Considering that a certain proportion of phosphorus was contained in many of the samples of iron and steel examined by the author, it was somewhat surprising that no indications of ferric phosphate or phosphoric acid should be found in any of the silica collected by this process; on the contrary, it was perfectly pure, volatilizing entirely under the influence of hydrofluoric acid. It became necessary therefore, to institute a more careful examination, and to ascertain exactly the manner in which the phosphorus was eliminated. To this end, some ferric phosphate was prepared in the ordinary way, mixed with a proportion of oxide, and placed in the same platinum vessel in which the previous analyses had been conducted; the tube having been brought to a bright-red heat, dry hydrochloric acid gas was passed

over it for two hours. At the expiration of this time the boat appeared empty; it contained, nevertheless, a few vitreous globules, which proved, on examination, to consist of sodium phosphate mixed with a little silica, the alkaline phosphate being doubtless a portion of that with which the iron was precipitated, and which had escaped washing. As far as regards the phosphoric acid combined with iron, the whole was volatilized, and found in the acid solution of iron contained in the flask at the extremity of the porcelain tube. In order to avoid the error introduced by the employment of artificial ferric phosphate, some finely-powdered vivianite was operated upon in the manner already described. In an hour the vivianite had disappeared, with the exception of a little earthy gangue, which contained neither iron nor phosphoric acid.

As a deduction from the foregoing experiments, it may be confidently stated, that when oxide of iron containing a small quantity of phosphoric acid is submitted to a current of hydrochloric acid gas, at a temperature sufficiently high to isolate the silica, the whole of the phosphoric acid is eliminated at the same time as the metal.

The following table shows the amount of silicon contained in various samples of iron and steel, as estimated by the dry method. The quantity of iron operated upon was one gram.

Swedish iron	0·00164
Puddled iron, from Unieux	0·00093
Bar iron	0·00190
Iron wire	0·00230
Cast steel	0·00070
Cast and cemented steel	0·00440
Chinese steel	0·00070
Soft steel	0·00093
Cast steel, for carriage springs	0·00094
,, for watch springs	0·00044
Cast steel, Krupp	0·00440
Tungsten steel	0·00093
Wootz steel	0·00062
Grey cast iron, from Ria	0·0140
White cast iron, from Ria	0·0034

J. W.

A New Method of Estimating Zinc. By Hugo Tamm.*

When a solution of zinc in any mineral or volatile organic acid is supersaturated with ammonia, then slightly acidulated with hydro-

* Chem. News, xxiv, 148—150.

chloric acid, a double chloride of zinc and ammonium is produced. The addition of hydro-disodic phosphate to the solution thus obtained occasions a precipitate of zinc phosphate, which, by subsequent heating in the liquid, combines with ammonium phosphate, thereby forming ammonio-zinc phosphate.

The author recommends this reaction for the separation and estimation of zinc, instead of the ordinary but very troublesome method of precipitating the zinc as sulphide. If great accuracy is required, the liquor should be left in a warm place for ten or twelve hours to ensure the complete precipitation of the zinc; but for ordinary assay purposes it is sufficient to allow the precipitate to rest for an hour.

The ammonio-zinc phosphate dried at 100° has the constant formula $Zn(NH_4)PO_4$. It is slightly soluble in water, and is converted by ignition into zinc phosphate, with loss of zinc. When formed as described, it retains sodium phosphate and ammonium chloride with some force, and several successive washings are required to free it from these salts.

Directions are given for estimating zinc in *spelter*, *blendes*, *calamines*, and *brass*. The general plan is as follows:—First, remove from the respective solutions all substances precipitable by sodium phosphate in a neutral or alkaline solution; saturate with ammonia; acidulate slightly with hydrochloric acid; add sodium phosphate in excess; heat near to boiling point; allow the liquid to remain in a warm place some time; collect; wash well with water; and dry at 100° C.

Most ammoniacal solutions of oxides, mixed with an excess of ammonia, are also precipitated by sodium phosphate, and when the mixture is boiled, the corresponding ammonio-phosphate crystallises.

Ammonio-manganese phosphate forms beautiful flesh-coloured crystalline silky scales.

Ammonio-cobalt phosphate forms crystals of an indifferent pink colour, which, when calcined at a low temperature, change to a deep blue colour, without losing the shape of the original crystals.

Ammonio-ferrous phosphate forms silky crystalline scales, resembling in colour certain greenish micas.

An examination of the ammonio-zinc phosphate has led the author to conclude that the equivalent of zinc is 32·75.

A. T.

On the Volumetrical Determination of Zinc by Sodic Sulphide.
By O. Schott.*

The author made some comparative experiments (1) with lead paper, prepared according to Fresenius's directions, by coating paper with

* Zeitschr. Anal. Chem. x, 209.

plumbic carbonate; (2) with cobalt-paper, prepared according to the directions of A. Deuss;* and (3) with a paper known in commerce as polka-paper, *i.e.*, ordinary glazed paper used for visiting cards covered with white lead; he gives the preference to the latter. The ammoniacal solution of zinc is placed in a beaker, diluted to half a litre, and sodic sulphide is run in as usual. The end of the reaction is ascertained by dipping into the liquid a glass tube 25 centim. in length and 7 mm. in diameter, wherewith a column of the liquid can be taken up by placing the thumb on the upper end of the tube. A piece of the glazed lead-paper is next pressed gently against the lower end of the tube held in a slightly slanting position over the beaker, and the liquid is allowed to run out slowly over the inclined card. The end of the reaction is indicated by the formation of a brown ring which appears where the liquid was brought in contact with the lead paper. The glass tube, the end of which should be first ground and then smoothed in the flame, should not be pressed too hard against the paper, in order to avoid any action of the suspended zinc sulphide upon the white lead.

The author claims a slight advantage for his indicator over that proposed by Fresenius, and a still more decided advantage over Deuss's indicator.

W. V.

Bromine-water as a Test for Phenol and Allied Substances.

By H. Landolt.†

In analysing the water of a well, situated in the neighbourhood of a gas work, the author was induced to search for phenol. The methods already known for detecting this body are only of a moderate degree of delicacy. The bluish-violet coloration with chloride of iron is but slightly sensitive, and is not always to be relied upon, since minute quantities of free acids, and even neutral salts, as potassium sulphate, sodium sulphate, &c., interfere with the reaction. The most satisfactory indications are afforded by bromine-water, which gives with a dilute solution of phenol an immediate yellowish bulky precipitate of tribromophenol. An excess of bromine-water must be employed. By this reaction 1 part of phenol in 43,700 parts of water may be easily detected. The limit to the chloride of iron reaction is 1 in 2,100 of water. The smell of phenol cannot be detected in a solution containing less than 1 part in 2,800 of water. The author shows that the precipitation by bromine-water may be employed for the quantitative determination of phenol. The same reaction will show the phenol present in urine.‡ 500 c.c. urine serve for its detection.

T. E. T.

* Zeitschr. Anal. Chem., ix, 165. † Deut. Chem. Ges. Ber., iv, 750—773.
‡ See also Lieben, Ann. Chem. Pharm. Suppl. Bd., vii, 740.

On the Methods for Determining the Amount of Alkaloïds in Peruvian Bark. By C. SCHACHT.*

THE author discusses at some length the respective advantages and disadvantages of the several methods for determining the alkaloïds in Peruvian bark, which have been recommended in various periodicals, as well as in the German and English pharmacopœas published during the last few years. The results which he obtained by these various methods differed widely (from ·95 p. c. to 8·67 p. c. of cinchona bases). Schacht fixed at last upon Hager's method,† which consists in converting the bases into picrates, decomposing with potassic hydrate, and extracting the free bases from the dried residue by means of absolute alcohol. The pulverised bark is first exhausted with water containing sulphuric acid, and the acid extract is precipitated by means of picric acid. 10 grms. of bark when so treated by the author gave ·6270 grm. of picrates; that is less than what Hager obtained. Instead of weighing the picrates as such, they may be decomposed by means of potassic hydrate. The mixture of potassic picrate and alkaloïds is then evaporated to dryness, and exhausted while warm with chloroform (free from alcohol), whereby a colourless filtrate is obtained; or it may be shaken up repeatedly with chloroform, the clear layer removed with a pipette, the chloroform distilled off, the residue taken up with water containing a little hydrochloric acid, and the bases precipitated with sodic hydrate. 10 grms. gave ·220 grm. of bases, equal to 2·2 per cent. Although this method was found to be preeminently quick and neat, the author was never able to obtain the quantity of picrates which Hager obtained. By substituting amylic alcohol for absolute alcohol, whilst proceeding in every other respect in the same manner, he obtained more favourable results—10 grms. of bark yielded 2·54 per cent. of bases. In a second experiment, in which the picrates were washed by decantation, decomposed by means of excess of potash-solution, and shaken up at once with amylic alcohol, he obtained 2·4 per cent. of bases. By modifying the process, so as to precipitate the bark-extract (obtained by boiling the finely macerated bark with solution of potash and sulphuric acid) at once with excess of solution of potash, without previously precipitating the bases as picrates, and extracting with amylic alcohol, he obtained 3·16 per cent. of bases. In his subsequent experiments, Schacht treated an aliquot part (50 c.c.) of the filtrate directly with 2·5 c.c. of potash of sp. gr. 1·3, and then with 25 c.c. of amylic alcohol, of boiling point 132° C. The layer containing the alkaloïds was drawn off with a pipette, and the extraction with amylic alcohol repeated three times over. In this manner he obtained in two experiments 3·16 and 3·12

* Arch. Pharm. [2], cxlvii, 97—106. † Pharm. Centralhalle, 1869, p. 145.

per cent. of bases. By allowing the mixture of 50 c.c. of bark extract, to which 2·5 c.c. of potash-solution and 25 c.c. of amylic alcohol had been added, to stand for twelve hours before pipetting off, and by shaking up three times more with amylic alcohol, the author obtained in three experiments 3·50, 3·52, and 3·82 p. c. of bases. In the last experiment the alkaloïds were found to be contaminated with a little colouring matter, carried down by precipitating with too strong a soda ley. Schacht usually prepared an extract from 10 grms. of bark, by boiling with solution of potash and sulphuric acid, made it up in a narrow cylinder to 110 c.c., and allowed it to subside sufficiently to obtain 50 c.c. of clear supernatant fluid, which could be filtered rapidly into a flask. Caustic potash is added, and, without any delay, amylic alcohol, and the whole well shaken up. The liquid separates speedily into two layers. The upper one, being very slightly coloured, is transferred by means of a pipette to a porcelain dish, wherein the portion of reddish-brown aqueous liquid subsides, before it is filtered through a small filter moistened with amylic alcohol into the distilling flask. The washing with amylic alcohol is effected in like manner, three times over. The amylic alcohol is next distilled off; the residue transferred from the flask to a small porcelain dish by rinsing with a little amylic alcohol (absolute alcohol has a tendency to creep over the dish and to cause a loss), and then evaporated to dryness. It is next *completely* taken up with water and a few drops of dilute sulphuric acid, of sp. gr. 1·16, and filtered cold through a small filter moistened with water. The precipitation of the bases is effected by means of *very dilute* caustic soda-solution (1 part of soda, of sp. gr. 1·3, to 9 parts of water), and continuous stirring, to prevent the balling of the precipitate. After standing quietly for some hours, it may be filtered through a weighed filter, and washed cautiously with very little water.

Addition of glycerin to the sulphuric acid extract of the bark did not yield favourable results. By dispensing, however, with the primary operation of treating the macerated bark with potash, in order to disintegrate the fibrous tissues, employing a mixture of 2 grms. of hydrochloric acid, of sp. gr. 1·12, together with 50 c.c. of glycerin, and 100 grms. of distilled water, and digesting the bark for 12 hours in the cold, a clear filtrate may be obtained, which not only passes freely through the filter, but leaves also a residue which can be washed out very readily. On evaporating the whole, the liquid remains invariably clear, and when treated with caustic potash and amylic alcohol, separates after some time into two layers, which can readily be removed from each other and washed. 3·41 per cent. and 3·72 per cent. of cinchona bases were obtained in this manner. It is, however, impossible to precipitate the bases as picrates, on account of their solubility in hydrochloric acid. W. V.

On a Method of Determining the Gases resulting from the Explosion of Nitroglycerin. By L. L. HOTE.*

To explode nitroglycerin, the author introduces a small quantity of it, from 5 to 6 milligrams, contained in small bulbs of thin glass, into a Mitscherlich's eudiometer, and then passes into the eudiometer a small quantity of electrolytic gas; on passing the electric spark, the explosion of this gas causes the detonation of the nitroglycerin. The gases formed, cause the mercury to turn brown on the surface. One gram. of nitroglycerin yields 284 cubic centimetres of gas at 0° C. and 760 mm., which contains 45·72 p.c. CO_2, 20·36 NO, and 33·92 N.

This method of explosion may be applied to the study of the gases furnished by other explosive compounds. Potassium picrate detonates easily under the conditions, and yields an inflammable gas containing an appreciable proportion of cyanogen.

A. P.

Technical Chemistry.

A New Method for the Separation and Utilisation of Phosphoric Acid in Iron Ores. By JULIUS JACOBI.†

THE author's process, patented in Bavaria in October, 1869, consists in treating iron ores containing phosphoric acid with sulphurous acid and water. The solution of the acid phosphate thus formed is evaporated and treated with quick lime and finally used as a manure. The sulphurous acid driven off in the evaporation may be collected and again used.

The author omits to mention the basic constituent of the insoluble phosphate contained in the ores to be treated in this way.

C. G.

On a New Process of Extracting Gold and Silver from their Ores. By L. E. RIVOT.‡

SHORTLY before his death, Rivot had been engaged in elaborating a process of treating Californian gold and silver-ores. This treatise being left in an unfinished state, was completed by Moissenet, and published in the Annales des Mines, 4 livraison de 1870, p. 1—104.

Rivot proposed to deal only with silver- and gold-bearing veins, not with gold occurring in soapstone and removed by washing. The gold veins to be worked may consist of quartz, or of quartz interspersed with sulphides and arsenides. The veins of silver ores occur in slate, quartz,

* Compt. rend., lxxiii, 1013. † Dingl. polyt. Journ., cci, 145.
‡ Berg. et Hüttenm. Zeitung, 1871, No. 32.

heavy spar, and calc-spar, containing the silver in combination with sulphur, with arsenic and sulphur, or with antimony and sulphur, and are accompanied by varying quantities of blende, galena, iron pyrites, arsenical pyrites, bournonite, fahlore, grey antimony, ore &c. The veins at Austin, 15 to 20 centim. in thickness, contain from 3 to 12 p. c. of silver, frequently also gold, especially the pyritical and arsenical veins. The processes employed at the present time in America for the extraction of gold and silver from mineral veins are: (1) The process of amalgamation in heaps; (2) amalgamation at 100° C. in copper pans; (3) direct amalgamation in pans by the aid of water, a process which is inexpensive, as it can be effected without material loss of mercury, but which does not yield so much gold and silver; and (4) amalgamation, preceded by the roasting of refractory ores with common salt. The yield of gold and silver from pyritical ores does not exceed 65 p. c. of the assay, which in itself is open to losses. According to many synthetical experiments, the loss is greater in assays of richer than of poor ores, amounting always to more than 30 p. c., and with fahlore and ores containing arsenical pyrites to more than 50 p. c. The loss incurred when working on a large scale is less than in laboratory assays. The difference between the yield on the large scale and the percentage indicated by the assay may exceed 30 p. c. when the metallurgical method is quite perfect; but as the American methods are far from perfect, the difference is still greater. Rivot's process, which was worked in California, gave good results, and is said to be applicable to ores of every kind, giving at small cost nearly the whole of the metal. It consists in roasting the ores with steam before amalgamation. Ores containing arsenic and antimony require an admixture of roasted iron pyrites. The experiments* made by Regnault and Cumenge on the roasting of sulphides, with simultaneous exposure to superheated steam, are quoted, and the experience gained by Rivot in California and Mexico, renders it apparent that superheated steam may be employed with advantage in extracting gold and silver from all ores, the action being somewhat sluggish in the case of pyrites and pyritical ores. It may be accelerated, however, by an admixture of oxidizing agents, such as ferric oxide, roasted pyrites, and black oxide of manganese, whereby the extraction of the gold and silver is rendered more effective. The process was found imperfect only in the case of copper ores containing arsenic and antimony, on account of these deleterious elements accumulating in the residues from the amalgamation process, and because the copper had to be given up as lost.

The author next describes in detail the different operations necessary, and the apparatus required in the many laboratory experiments

* The labours of Patera and Marcus, but especially those of Plattner, appear to have been unknown to the compiler of Rivot's notes.—W. V.

which he made, as well as those required to carry out the process on the large zcale, viz. :—

1. Roasting of the pyrites in heaps, or in reverberatory furnaces, in such a manner as to almost completely oxidize the metallic sulphides, and to reduce the formation of sulphates to a minimum.

2. Pulverizing and mixing of the roasted pyrites with the ores.

3. Roasting of the mixed mass with superheated steam in a revolving furnace, with exclusion of air.

4. Amalgamation in vertical mills, which are capable of a great out-turn, and of working wet or dry, as may be desired, and which divide the mercury well, and effect a more speedy and complete amalgamation, owing to the pressure of the millstones.

5. Separation of the mercury from the residues.

6. Squeezing of the mercury through coarse linen bags, or wooden cylinders.

7. Distillation of the amalgam in cast-iron tubes provided with receivers cooled by water.

8. Smelting of the metals recovered by amalgamation in blacklead crucibles, and casting in iron moulds.

W. V.

On Cobalt Ultramarine. By W. Stein.*

To prove still further (comp. p. 166 and 850) that cobalt ultramarine is a *mixture* of aluminic silicate with $4CoO.Co_2O_3$, the author examined a sample of cobalt ultramarine, which was entirely free from arsenic, and contained only traces of phosphoric acid. The existence of a higher oxide of cobalt could be established only by heating in a current of hydrogen gas at the temperature of a Mitscherlich's furnace. A sample of previously ignited ultramarine lost 6·78 p. c. of oxygen, and left a black residue. By fusing in a silver crucible with pure caustic potash and extraction with water, the cobalt oxide (probably in combination with potash as cobaltic acid Co_2O_3) can be readily separated from the alumina and silica, and may be freed from potash in the usual manner, and weighed as metallic cobalt. The percentage composition of the ultramarine was thus found to be—silica, 4·00; alumina, 68·45; cobalt, 20·80; oxygen, 6·75. The oxide, $4CoO.Co_2O_3$, requires 6·58, that of $CoO.Co_2O_3$ 7·52, of oxygen, hence it contained about four parts of the former to one of the latter oxide, *i.e.*, an oxide such as is obtained by igniting cobaltous oxide with free access of air. A further proof for the theory that cobalt ultramarine is a mere molecular mixture, was furnished by a synthetical experiment. Ordinary black cobaltic oxide was intimately mixed with pure alumina, and the mixture ignited,

* Dingl. polyt. J., cci, 420.

whereby blue ultramarine was obtained. In order to succeed it is necessary that the alumina should be perfectly loose, the mixture made as intimate as possible, and that a vivid red heat should be applied for a sufficient length of time.

W. V.

On J. Schweiger's New Painting Ground for Stereochromic Pictures. By Dr. Feichtinger.*

The ground recommended by Pettenkofer (cement and sand) possesses all the qualities required, such as regular absorptive power, durability, &c., but not being white is not regarded favourably by painters. Schweiger's ground was devised in order to obviate this inconvenience. It consists of carbonate of lime, cement, and quartz sand, mixed with a solution of *potash* water-glass, of which so much is added that the mass can be laid on with a brush, and in greater quantity the more porous the ground is. The carbonate of lime may be either chalk or marble powder; the quartz-sand must be clean and well washed, and of even grain. The mass of carbonate of lime and quartz-sand together should be 3—4 times the volume of the cement.

C. H. G.

Process for Preparing Anthracene from Coal-tar Pitch, and Preparation of Dye-stuffs from Anthracene. By J. Brönner and H. Gutzhow.†

The pitch is distilled in gas-retorts with help of superheated steam.

Anthracene is treated with twice its weight of nitric acid of 1·3—1·5 sp. gr., cold or warm. The new product is washed by water and dissolved, with or without purification, in the required quantity of warm sulphuric acid, and treated with the necessary amount of mercurous or mercuric nitrate. After the colouring matter has formed, it is taken up by some solvent, such as cold or boiling water, or alcohol, ether, carbon sulphide, alum solution, dilute alkalies, &c.; the solution is evaporated or precipitated by acids, and purified by crystallisation from solution, or by sublimation.

For the preparation of alizarin from anthracene, the authors follow an improved process. The anthracene is converted into oxanthracene, which is then purified by sublimation. The latter is converted into alizarin by heating to 200°—250° C. with twice its weight of concentrated potash- or soda-ley, and after the termination of the reaction, is precipitated from the solution of the mass by addition of an acid. The alizarin is then washed.

C. H. G.

* Dingl. polyt. J., cci, 541—544. † Dingl. polyt. J., cci, 545.

On the Influence of the Secondary Extract Formation in Fermenting Mashes. By W. SCHULTZE. (Dingl. Polyt. J. cci, 438—461.)

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*Action of Chromate of Potash on Thickening Materials.**

WHEN a mixture of gum, dextrin, &c., with chromate of potash is used for discharging colours, it sometimes happens that washing will not leave the pattern white. This arises from the fact that such a mixture when exposed to light becomes partly insoluble, and consequently cannot be entirely removed from the cloth. The remedy is to work in rooms having yellow glass windows.

C. H. G.

On Rose-napthalene, or Magdala Red. (Dingl. Polyt. J. cci, 468.)—Directions for dyeing silk with this colour.

A Fast Sulphur Black. (Dingl. Polyt. J. cci, 468.)

On the Application of Disinfecting Powders containing Carbolic Acid. (Dingl. Polyt. J. cci, 470.)

On Certain Applications of Bisulphide of Carbon. By H. HAEDICKE. (Dingl. Polyt. J. cci, 427—432.)

A Colorimeter. By H. RHEINECK.†

TWO thick glass plates, touching at one end and separated at the other by a platinum wire. The lower plate is engraved with a scale.

The intensity of colour in a solution is measured by introducing a few drops of liquid between the plates, and observing at what point of the scale the lines below become invisible through the liquid. It was devised for measuring the opacity of milk.

C. H. G.

Ensom and Spence's Process for Wool Washing and Dyeing. By C. BOLLE.‡

THE wool is thoroughly mixed with the washing solutions and dye-liquors, by blowing compressed air through the vats in which the operations are performed. The advantages of the process are saving of labour, completeness of the washing, and saving of chemicals and dye stuff. Working details are given.

C. H. G.

* Dingl. polyt. J., cci, 467. † Dingl. polyt. J., cci, 433.
‡ Dingl. polyt. J., 435—438.

Note upon the Composition of French and other Beers Consumed in Paris. By E. MONIER.*

THESE beers may be divided into two classes, first, bitter beers, or those of the north of France, England, and Belgium; second, sweet beers, principally from Germany and Austria.

Composition in 1,000 *grams.*

	From	Alcohol by vol. (c.c.)	Glucose. (grams.)	Dextrin albuminoid substances,&c. (grams.)	Salts. (grams.)
Bitter beers.	North France	40·0	7·03	31·77	1·6
	,, ...	32·5	4·8	31·0	2·1
	,, ...	36·0	6·6	33·1	2·2
	Burton (pale ale).....	60·5	8·25	39·35	2·8
	,, ,, ...	55·0	8·3	40·1	2 65
Sweet beers.	Munich.....	56·25	15·1	58·4	2·52
	,, ...	56·5	16·2	56·45	2·4
	Vienna	52·5	11·0	55·3	2·3
	Amsterdam	53·75	13·55	51·5	2·2
	Paris (called Strasburg)..	47·0	16·3	45·0	2·65
	,, ,, ..	45·0	14·35	51·3	2 05
	,, ,, ..	47·5	11 60	43·4	2·0

When the large quantities of glucose and dextrin found in the German beers have been obtained by the action of diastase upon starch, they have no hurtful effect upon the human system. These substances, however, are oftener produced by the action of sulphuric acid upon starch, in which case the beer is more difficult of digestion, producing thirst, and often provoking bronchial affections. In beers to which glucose has been added, the amount of sulphates sometimes rises to 1·5 grams per litre, the quantity present in natural beers being from 4 to 20 centigrams only.

J. B.

* Compt. rend., lxxiii, 801.

A LIST

OF THE

OFFICERS AND FELLOWS

OF

THE CHEMICAL SOCIETY.

LONDON:
HARRISON & SONS, ST. MARTIN'S LANE,
Printers in Ordinary to Her Majesty.

MDCCCLXXI.

CHEMICAL SOCIETY,

FOUNDED IN FEBRUARY, 1841; INCORPORATED BY ROYAL CHARTER, 1848.

THE Meetings of the Society, for the reading and discussion of scientific papers, are held on the first and third Thursdays of every month, from November to June inclusive, excepting that in January there is only one Meeting, on the third Thursday of the month. The Chair is taken at eight o'clock precisely.

An Annual General Meeting is held on the 30th day of March (or if that day fall upon Sunday, on the 31st) at eight o'clock P.M., for the Election of Officers for the year ensuing, and for receiving the Report of the Council on the state of the Society.

Fellows of the Society have the right to be present, and to vote at all Meetings of the Society; to introduce two visitors to the ordinary Meetings; and to receive the Transactions published during the period of their continuing Fellows. They are also entitled to the use of the Books in the Society's Library, under such restrictions as the Council shall deem necessary.

Candidates for admission into the Society are proposed according to a form of recommendation, which may be obtained from the Secretaries. The recommendation must be signed by five Fellows, to three at least of whom the candidate shall be personally known; and such certificate is to be read and suspended in the Society's rooms for three ordinary Meetings before proceeding to ballot for the election.

Burlington House, Piccadilly, W., 1871.

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Feb. 7, 1843	‖De la Rue, Paul, Esq., Ekateringoff, near St. Petersburgh
Feb. 23, 1841	‖*De la Rue, Warren, D.C.L., F.R.S., Observatory, Cranford, Middlesex, W.
Mar. 16, 1857	Dent, W. Y., Esq., Royal Arsenal, Woolwich, S.E.
June 2, 1859	De Rheims, Henry, Esq., 1 and 2, Vicarage-park, The Common, Plumstead, S.E.

Date of Election.	
Dec. 1, 1870	Dewer, James, Esq., Veterinary College, Edinburgh
Dec. 6, 1866	‖Dircks, Henry, Esq., Whitehall Club, S.W.
Feb. 2, 1860	Divers, Edward, M.D., 16, Bevington-road, Notting-hill, W.
Dec. 18, 1862	Dixon, W. A., Esq., 25, Gordon-street, Glasgow
Mar. 5, 1868	‖Dowson, Dr. Edward, 117, Park-street, Grosvenor-square, W.
Mar. 17, 1859	Draper, Harry, N., Esq., 72, Leinster-road, Rathmines, Dublin
Feb. 23, 1852	Dresser, Christopher Leefe, Esq., Leeds
May 1, 1854	‖Duffy, Patrick, Esq., Surveying General Examiner Office, Inland Revenue, Somerset House, W.C.
Dec. 17, 1863	Duncan, James, Esq., 5, Highbury-hill, N.
Feb. 16, 1860	Dupré, Frederick, Ph.D., 53, Burton-crescent, W.C., and Stassfurt, Prussia
Jan. 19, 1860	Dupré, Auguste, Ph.D., 53, Burton-crescent, W.C., and Westminster Hospital
Dec. 17, 1863	Duppa, B. F., Esq., F.R.S., United University Club, Pall Mall East
June 1, 1871	Durham, Henry, 24, Gordon-road, Stoke Newington
Feb. 7, 1848	‖Edwards, John B., Ph.D., Royal Institution, Liverpool
Dec. 1, 1864	Ekin, Charles, Esq., Bath
May 1, 1862	‖Esson, William, Esq., Merton College, Oxford
Feb. 2, 1865	‖Estcourt, Charles, Esq., Inland Revenue Office, Bristol
Nov. 5, 1849	Evans, Henry Sugden, Esq., 60, Bartholomew-close, E.C.
Feb. 21, 1867	Eve, H. W., Esq., Wellington College, Wokingham, Berks
May 18, 1865	Fairley, Thomas, Esq., Grammar School, Leeds
Dec. 1, 1870	Farries, Thomas, Esq., 16, Coleman-street, E.C.
Feb. 4, 1864	‖Ferreira, A. A., M.P.S., Rio de Janeiro, Brazil
April 21, 1859	Fewtrell, William Toplady, Esq., 41, Gower-place, Euston-square, W.C.
Dec. 5, 1867	Fiddes, W. W., Esq., Clifton Villa, Clifton Wood, Bristol
June 18, 1857	Field, Henry W., Esq., M.A.P.S.Phil., Royal Mint, E.
Dec. 21, 1846	Field, Frederick, Esq., F.R.S., 9, Belmont-park, Lee, S.E.
Feb. 4, 1869	‖Field, James John, Esq., Highgate, N.
June 15, 1871	Finkelstein, B., Bad. Anilin and Soda Fabrik, Ludwigshafen, am Rhein.
Dec. 7, 1865	FitzHugh, Richard, Esq., Nottingham
Dec. 19, 1867	Fletcher, A. E., Esq., 21, Overton-street, Liverpool
June 7, 1866	Flower, W. F., Esq., Infirmary, Leicester.
June 16, 1859	Fogg, Thomas, Esq., 11, Lanark-villas, Clifton-road, Maida-hill, W.
Feb. 21, 1853	Foord, G., Esq., Australia
Feb. 21, 1853	‖Forbes, David, Esq., F.R.S., 11, York-place, Portman-square, W.
Dec. 6, 1866	Forrest, James, Esq., 7, Park-cottages, Maize-hill, Greenwich, S.E.
April 6, 1865	Foster, Dr. M., jun., Trinity College, Cambridge.
Mar. 3, 1856	Foster, G. C., Esq., F.R.S., University College, W.C.
Feb. 17, 1870	Francis, E., 22, St. Peter's-square, Hammersmith, and Charing Cross Hospital
Nov. 7, 1842	Francis, William, Ph.D., F.L.S., Red Lion-court, Fleet-street, E.C.
Dec. 20, 1847	‖Frankland, E., D.C.L., F.R.S., 14, Lancaster-gate, Hyde-Park, W.
Mar. 21, 1867	Fraser, Dr. Angus, 193, Union-street, Aberdeen
Mar. 7, 1867	Freeman, J. Hersee, Esq., Stratford-house, Stratford, E.
Feb. 2, 1871	Friswell, R. J., Esq., 74, Great Russell-street, Bloomsbury, W.C.
April 19, 1866	Gale, James, Esq., Buckfast Abbey, Buckfastleigh, South Devon.
April 5, 1852	‖Gale, Samuel, Esq., 338, Oxford-street, W.
Dec. 20, 1847	Galloway, Robert, Esq., Royal College of Science, Stephen's-green, Dublin
Mar. 17, 1851	‖Gamble, David, Esq., Gerard's-bridge, St. Helens, Lancashire
June 21, 1866	Gamgee, Arthur, M.D., F.R.S.E., Lecturer on Physiology at Surgeon's Hall, Edinburgh, and Physician to the Royal Edinburgh Hospital for Sick Children, 27, Alva-street, Edinburgh
Feb. 23, 1841	*Gassiot, John Peter, F.R.S., Clapham-common, S.

Date of Election.	
Jan. 18, 1847	Gatty, F. A., Esq., Holland Bank, Accrington, Lancashire
Feb. 18, 1864	Gibbons, Sydney, Esq., Collins-street East, Melbourne
Dec. 9, 1869	Gibbs, Thomas, Esq., Bede Metal Company, Jarrow-on-Tyne
May 18, 1841	Gilbert, Joseph Henry, Ph.D., F.R.S., Harpenden, near St. Albans
April 3, 1862	Gill, C. Haughton Esq., 50, King Henry's-road, N.W.
Dec. 18, 1848	Gladstone, John Hall, Ph.D., F.R.S., 17, Pembridge-square, Hyde park, W.
Nov. 3, 1851	Gladstone, George, Esq., Clapham-common, S.W.
May 21, 1849	Glass, William, Esq., 10, Ashmead-road, New Cross
Dec. 4, 1862	Gossage, William, Esq., West Bank, Widnes Dock, near Warrington
Feb. 2, 1871	Gowland, William, Esq., 4, Olive-terrace, Stretford, Manchester.
May 1, 1862	‖Graham, Charles, Esq., D.Sc., University College, W.C.
Feb. 19, 1863	Green, Joseph, Esq., Messrs. Sang and Basker's, Manufacturing Chemists, Barony-street, Edinburgh.
May 18, 1871	Greenish, Thomas, F.R.N.S., 20, New-street, Dorset-square
Jan. 16, 1868	Griess, Peter, Esq., F.R.S., Messrs. Allsops & Sons, Burton-on-Trent
Feb. 23, 1841	*Griffin, John Joseph, Esq., 22, Garrick-street, Covent-garden, W.C.
June 16, 1859	Griffith, George, Esq., Peterborough-road, Harrow.
May 2, 1861	Griffith, Thomas, Dr., 12A, Surrey-street, Sheffield
Feb. 2, 1871	Grosjean, B. J., Esq., 97, Euston-road, N.W., and Atlas Chemical Works, Millwall
Dec. 17, 1857	Groves, T. B., Esq., Weymouth
April 6, 1871	Groves, Charles, Esq., 80, Upper Kennington-lane, S.E.
April 20, 1871	Grundy, Cuthbert C., Esq., Bankfield near Bury, Lancashire.
April 2, 1868	Guthrie, Frederick, Ph.D., F.R.S., F.R.S.E., Royal School of Mines, Jermyn-street, S.W.
Feb. 3, 1859	Hake, T. Gordon, M.D., Coombe End, Roehampton, S.W.
Dec. 4, 1862	Hall, T. F., Esq., 29, Warwick-square, S.W.
May 3, 1866	‖Hall, Marshall, Esq., 3, Cleveland-terrace, Hyde-park, W.
Dec. 5, 1867	Hall, Thomas, Esq., B.A., 14 and 15, the Hard, Portsea, Hants
Feb. 3, 1859	‖Hambley, C. H. Burbidge, Esq.
Nov. 15, 1852	Hamilton, George, F.R.A.S., Queen's College, Liverpool
Feb. 7, 1857	Hanbury, Cornelius, jun., Esq., Plough-court, Lombard-street, E.C.
Jan. 21, 1858	‖Hanbury, Daniel, F.R.S., F.L.S., Plough-court, Lombard-street, E.C.
Feb. 3, 1859	‖Harcourt, A. Vernon, Esq., M.A., F.R.S., Christchurch, Oxford
April 16, 1853	‖Harcourt, L. Vernon, Esq., Harbour of Refuge, Alderney
Mar. 2, 1857	‖Harley, George, M.D., F.R.S., 25, Harley-street, Cavendish-square, W.
March 2, 1871	Harding, G. D., Esq., Askham-in-Furness, Lancashire
June 20, 1861	Harris, W. H., Esq., Laboratory, Long Buckly Wharf, near Rugby
Nov. 2, 1869	Harrison, George, Ph.D., F.C.S., 265, Glossop-road, Sheffield
Jan. 21, 1869	Hart, F. W., Esq., 8, Kingsland-green, London
Dec. 20, 1866	Hartley, Walter Noel, Esq., King's College, W.C.
May 5, 1856	Harvey, Alexander, Esq., Govanhaugh Dye Works, Glasgow
Nov. 20, 1848	Hay, W. J., Esq., 3, Powis-gardens, Albert-road, Bayswater, N.W
Dec. 1, 1864	Heywood, Henry, Esq., Cardiff
Feb. 21, 1867	Hearder, Jonathan Nash, Esq., Ph.D., 195, Union-street, Plymouth
April 20, 1865	Heathfield, W. E., Esq., F.R.S.E., 20, King-street, St. James's, S.W.
Dec. 18, 1854	Heaton, Charles W., Esq., Charing-cross Hospital, W.C.
Feb. 23, 1841	*Heisch, Charles, Esq., Middlesex Hospital, W.
April 4, 1861	Henn, Rev. John, B.A., Lond., F.R.G.S., Commercial School, Manchester
Mar. 7, 1853	‖Henry, W. C., M.D., F.R.S., Haffield, near Ledbury
Feb. 21, 1853	Hepburn, J. G., LL.B., 16, Long-lane, Bermondsey, S.E., and Reform Club, S.W.
Feb. 16, 1871	Herman, Douglas, Esq., St. Ann's, St. Helen's, Lancashire
April 3, 1848	Heywood, J. S. C., Esq., 13, Hanover-villas, Kensington Park, Notting-hill
Mar. 15, 1852	Higgin, James, Esq., B.A., 22, Little Peter-street, Manchester

Date of Election.	
Jan. 20, 1870	Higgins, Clement, Esq., B.A., 27, St. John's-park, Upper Holloway
Dec. 16, 1858	Hill, Alfred, M.D., Laboratory, Queen's College, Birmingham
Feb. 7, 1853	Hills, Frank C., Esq., Chemical Works, Deptford, S.E.
Mar. 18, 1858	‖Hills, Thomas Hyde, Esq., 338, Oxford-street, W.
April 15, 1858	Hindle, James, Esq., Sabden, Whalley, Lancashire
Jan. 20, 1870	Hislop, G. R., Esq., Gasworks, Blackstoun-road, Paisley
April 6, 1865	‖Hobson, A. S., Esq., 3, Upper Heathfield-terrace, Turnham-green, W.
Mar. 4, 1858	Hobson, J. T., Ph.D., Laurel House, Tyldesley, near Manchester
	Hodges, John F., M.D., Queen's College, Belfast
Mar. 3, 1849	‖Hofmann, Aug. Wm., D.C.L., F.R.S., Prof., 10, Dorothien Strasse, Berlin
Feb. 18, 1869	Holditch, E. D., Esq., 10, Bankside, Southwark, S.E.
May 4, 1865	Holzmann, M., Ph.D., Marlborough-house, S.W.
Dec. 18, 1862	Hooker, John, Esq., Dean's-place West, Husley, Woking Station, Surrey
Dec. 9, 1869	Hopwood, G. Manly, Esq., Messrs. Pochin & Co., Quay-street, Salford, Manchester
Dec. 15, 1856	Horsley, John, Esq., Cheltennam
Feb. 18, 1869	Howard, Alfred K., Esq., Messrs. Muspratt Bros. and Huntley, Flint, North Wales
Nov. 3, 1870	Howard, David, Esq., Stamford-hill, N.
Dec. 20, 1842	Howard, Robert, Esq., Stratford, Essex, E.
Feb. 16, 1871	Houlder, W. W., Esq., Southall, Middlesex, and 2 St. John's-terrace, Southall-green, Southall
Feb. 6, 1868	Hozier, Capt. J. W., Junior United Service Club, Charles-street, St. James's, S.W., and Cavalry Brigade Office, Aldershot
March 2, 1871	‖Hudleston, W. H., M.A., F.G.S., 23, Cheyne-walk, Chelsea
Feb. 7, 1867	Hudson, J. W., LL.D., Somerleyton, Brixton, S.
April 19, 1866	Huggon, William, Esq., Park-row, Leeds
Feb. 23, 1841	*Hughes, F. R., Esq., Bo'ness, Linlithgowshire
Dec. 17, 1868	Hughes, John, Esq., 16, Penn-road-villas, Camden-road, Holloway, N.
Jan. 19, 1871	Humiston, Ransom Franklin, M.A., M.D., late President of Cleveland Institute, Ohio, U.S. America
Mar. 18, 1869	Hunt, Charles, Esq., London Gas Light Company, Nine Elms, S.W.
Dec. 15, 1851	Hunt, Edward, Esq., 6, Mouton-terrace, Moss-side, Manchester
Dec. 7, 1865	‖Hunter, John, Prof., M.A., F.C.S., Queen's College, Belfast
Mar. 21, 1861	Huskisson, H. O., Esq., 322, Gray's-inn-road, W.C.
Dec. 6, 1866	Huskisson, William, jun., Esq., 76, Swinton-st., Gray's-inn-road, W.C.
June 18, 1863	Hutchinson, Rev. T. N., Hillmorton-road, Rugby
Feb. 7, 1867	‖Ince, Joseph, Esq., 10, Vigo-street, Regent-street, W.
Dec. 16, 1869	Jefferson, S., Esq., 18, Caledonian-road, Leeds
Dec. 18, 1843	Jennings, Thomas, Esq., 10 and 11, Brown-street, Cork
May 6, 1858	Johnson, Richard, Esq., 27, Dale-street, Manchester
May 19, 1866	Johnson, Samuel L. Alton, Esq., Elwick Ham, Frith-road, Stratford, Essex
May 11, 1841	‖Jones, Henry Bence, M.D., F.R.S., 31, Brook-street, Grosvenor-square, W.
Feb. 2, 1857	Jones, John, Esq., 16, Adelaide-terrace, Portishead, Somerset
Dec. 15, 1856	Jones, Hodgson, Esq., 67, Victoria-street, Westminster, S.W.
Mar. 16, 1865	Jones, George, Esq., 106, Leadenhall-street, E.C.
April 6, 1871	Jones, E. W. T., Esq., Pennfields, Wolverhampton, and 10, Victoria-street, Wolverhampton
Jan. 1, 1844	Joule, James P., F.R.S., 5, Cliff-point, Higher Broughton, near Manchester
April 6, 1865	Judd, William, Esq., 10, Bath-street, Leamington
Mar. 4, 1858	‖Kane, Sir Robert, F.R.S., 51, Stepnen's-green, Dublin
June 2, 1856	Kay, William, Rev., B.A., 8, Salisbury-street, Liverpool
Nov. 4, 1869	Keightley, W. F., Esq., Old-hall, Milnthorpe, Westmorland

Date of Election.	
April 4, 1867	‖Kemp, David Skinner, Esq., Bombay
May 18, 1857	Kensington, Edward Thomas, Esq., 9, Albert-terrace, Mount Radford, Exeter, Devon
May 4, 1865	Kirkham, Thomas Nesham, Esq., Cambridge Villa, Gilston-road, West Brompton
June 16, 1864	Knox, G. W., Esq., B.Sc., 11, East-parade, Sheffield
Dec. 15, 1870	Koma, Reinoska, Esq., University College, W.C.
Feb. 17, 1859	Kynaston, Josiah W., Esq., St. Helens, Lancashire
Feb. 3, 1859	‖Lackersteen, Mark Henry, M.D., M.R.C.P., F.L.S., F.Z.S., F.R.G.S., F.C.S., 29, Queen Anne-street, Cavendish-square, W.
Feb. 4, 1864	Lambert, Charles, Esq., 3, Queen-street-place, Upper Thames-street, E.C.
Mar. 3, 1859	Lansdell, Mark J., Esq., 38, Gracechurch-street, E.C.
Jan. 20, 1870	Lapper, Edwin, Esq., Demonstrator of Chemistry, Ledwick School of Medicine, Peter-street, Dublin
June 17, 1850	‖Lawes, John Bennet, F.R.S., Rothamsted, near St. Albans
April 20, 1871	Lee, J. Bridges, B.A., F.Z.S., F.G.S., Sidney Sussex College, Cambridge, and 115, Ledbury-road, Westbourne-park, Bayswater, W.
Feb. 23, 1841*	‖Leeson, H. B., M.D., F.R.S., Bonchurch, Isle of Wight
Mar. 17, 1859	Letheby, Henry, M.B., 17, Sussex-place, Regent's-park
Nov. 18, 1869	‖Lewis, W. J., Esq., Oriel College, Oxford
June 21, 1866	Lightbown, J. H., Esq., care of R. Lightbown, Pernambuco, Brazil
May 16, 1861	Lindsay, Thomas, Esq., 288, Renfrew-street, Glasgow
Nov. 21, 1853	‖Liveing, G. D., Esq., M.A., Cambridge
Feb. 16, 1871	Lockyer, George, Junior, Esq., 21, Mincing-lane, E.C., and the Grove, Boltons, S.W.
Feb. 16, 1871	Lockyer, William John, Esq., 21, Mincing-lane, E.C., and Pembroke Villa, Elgin-park, Redland, Bristol
Feb. 23, 1841	*Longstaff, George Dixon, M.D., Southfields, Wandsworth, S.W., and 9, Upper Thames-street, E.C.
Dec. 15, 1856	Lowe, Charles, Esq., Smethwick-hall, Brereton, near Congleton, Cheshire
June 16, 1870	Lucas, Lewis Arthur, Esq., 46, Westbourne-terrace, Hyde-park
May 3, 1866	Lundy, J. J., Esq., F.G.S., Leith
Dec. 5, 1867	Lunge, Dr. George, Westoe-crescent, South Shields
Feb. 3, 1859	‖Lyte, F. Maxwell, Esq., Bagnéres de Bigorre, Hautes Pyrénées, France
Feb. 21, 1853	Macadam, Stevenson, Ph.D., F.R.S.E., Surgeons'-hall, Edinburgh
Dec. 18, 1862	Machattie, A. T., M.D., 1, Stanley-street, Glasgow
April 4, 1867	Mackay, John, Esq., 119, George-street, Edinburgh
Jan. 15, 1844	Maclagan, Douglas, M.D., F.R.S.E., School of Medicine, Surgeons'-hall, and 28, Heriot-row, Edinburgh
April 21, 1864	Mactear, James, Esq., St. Rollox, Glasgow
Feb. 16, 1871	Mayer, J. E., M.D., 3, Cambridge-terrace, Junction-road, Kentish-town, N.W.
April 5, 1866	McCalmont, Robert, Esq., Messrs. Ritchie and Sons, Belfast
April 19, 1860	McDonnell, John, Esq., Clare-villa, Upper Rathmines, Dublin
Dec. 17, 1857	McDougall, Alexr., Esq., Barco Lodge, Penrith
Feb. 6, 1871	McEwen, Lawrence F., Esq., Lombard House, 56, Lombard-street, E.C.
Feb. 6, 1868	McLeod, Herbert, Esq., Indian Civil Engineering College, Cooper's Hill, Egham
May 1, 1862	Madan, H. G., Esq., Eton College, Windsor
Mar. 17, 1845	Makins, Geo. H., Esq., Danesfield, Walton-on-Thames
Dec. 17, 1857	Mallet, J. W., Ph.D., 7, Westminster-chambers, Victoria-street, S.W.
Dec. 1, 1870	Mallet, Robert, C.E., F.R.S., 7, Westminster-chambers, Victoria-street, S.W., and Enmore, The Grove, Clapham-road, S.
Feb. 4, 1858	‖Manning, F. A., Esq., 18, Billiter-street, E.C.
Feb. 7, 1853	Marcet, W., M.D., F.R.S., 48, Harley-street, W.
Dec. 6, 1866	Marreco, A. F., Esq., Laboratory, College of Medicine, Newcastle-on-Tyne

Date of Election.	
Nov. 16, 1865	Marriott, William, Esq., Grafton-place, Huddersfield
April 7, 1870	Martindale, William, Esq., University College Hospital, W.C.
June 1, 1871	‖Martineau, George, Esq., Walton-on-Thames, Weybridge
June 2, 1851	Maskelyne, Nevil Story, Esq., F.R.S., British Museum, W.C.
Mar. 2, 1871	Mason, Alfred Henry, Esq., 317, Upper Parliament-street, Liverpool
Nov. 4, 1858	‖Mason, James, Esq., Eynsham Hall, near Witney, Oxon
Jan. 16, 1868	Mason, W. G., Esq., Kennell Hall, Killinghall, Ripley, Yorkshire
May 3, 1870	Matthey, George, Esq., 78, Hatton-garden, E.C.
Mar. 6, 1862	Mathews, F. C., jun., Esq., Driffield
Feb. 17, 1859	‖Matthews, Henry, Esq., 60, Gower-street, Bedford-square, W.C.
Dec. 7, 1865	‖Maxwell, Theodore, Esq., High Roding Rectory, Dunmow, Essex
May 18, 1871	Mayall, J. E., Esq., Hove-place House, Brighton
Dec. 5, 1867	Maybury, Charles Walter, Esq., 90, King-street, Manchester
Mar. 20, 1862	Mayer, John, Esq., 2, Carlton-place, Glasgow
Dec. 16, 1850	‖Medlock, Henry, M.D., 26, Charles-street, St. James's, S.W.
Feb. 16, 1871	Meldola, Raphael, Esq., 21, John-street, Bedford-row, W.C.
	Meldrum, Edward, Esq., Dechmont, by Broxburn, N.B.
Jan. 18, 1847	Mercer, John, Esq., Oakenshaw, Blackburn, Lancashire
Feb. 18, 1856	Mercer, Nathan, Esq., Apothecaries' Hall, Montreal
May 6, 1869	Meusel, Dr. E., 2, An der Saukirch, Breslau
Dec. 4, 1862	Michael, W. H., Esq., Cholmeley-park, Highgate, N.
May 20, 1844	‖Middleton, J., Esq., 27, Eastbourne-terrace, Paddington, N.W.
Dec. 18, 1843	‖Millar, James, Esq., William Brown, Esq., 87, St. Vincent-street, Glasgow
June 4, 1868	Miller, F. B., Esq., Royal Mint, Melbourne, Australia
Feb. 23, 1841	*Miller, Wm. Hallows, Esq., M.A., F.R.S., Scroope-terrace, Cambridge
Dec. 18, 1862	Mills, E. J., Esq., D.Sc., 12, Pemberton-ter., St. John's-park, London, N.
Feb. 18, 1864	Morfit, Campbell, Ph.D., Sudbrook Park, Petersham, Surrey
Nov. 4, 1869	Morrison, John, Esq., Forth Bank Chemical Works, Newcastle-upon-Tyne
Dec. 15, 1851	Morson, Thomas, jun., Esq., 124, Southampton-row, Russell-square, W.C.
Jan. 19, 1871	Moss, John, Esq., Pharmaceutical Society, Bloomsbury-square
Jan. 19, 1871	Moss, R. J., Esq., 2, Fortfield-terrace, Rathmines, Dublin
May 6, 1869	Muir, J. M., Esq., Assay Office, Union Bank of Australia, Thames Goldfields, Grahamstown, Auckland, New Zealand
Feb. 16, 1871	Muir, M. M. P., Esq., 12, Woodlands-terrace, Glasgow
Feb. 3, 1859	‖Müller, Hugo, Ph.D., F.R.S., 110, Bunhill-row, E.C.; and Woburn Lodge, Upper Woburn-place, W.C.
Dec. 9, 1869	Murchison, Sir R. I., Bart., F.R.S., Belgrave-square, S.W.
Feb. 20, 1868	‖Murphy, Martin, Esq., College of Chemistry, Duke-street, Liverpool
Dec. 18, 1848	Muspratt, F., Esq., 21, Westmoreland-place, Bayswater, W.
Jan. 15, 1863	Muspratt, J. L., Esq., Widnes, near Warrington
Jan. 21, 1869	‖Muspratt, E. K., Esq., Seaforth Hall, near Liverpool
Dec. 18, 1843	‖Muter, Andrew, Esq., Milton, Dumbartonshire
Nov. 3, 1870	Muter, John, Esq., South London Analytical Laboratory, 289, Kennington-road, S.
Dec. 18, 1848	Napier, James, Esq., Vinegar Hill Chemical Works, Camlachie, Glasgow
	Neild, Alfred, Esq., Mayfield, Manchester
June 1, 1871	Neison, Edmund, Esq., 37, Fellows-road, Eaton-park, N.W.
April 19, 1860	Newlands, J. A. R., Esq., 13, Knowle-road, Brixton, S.
Feb. 18, 1864	Newlands, B. E. R., Esq., 4, Malvern-terrace, Victoria-road, Charlton, S.E.
May 15, 1848	Nicholson, E. Chambers, Esq., Herne-hill, S.
Mar. 2, 1871	Nicholson, John Joseph, Sunderland
Feb. 15, 1866	Nickels, Benjamin, Esq., 114, Victoria Park-road, South Hackney, N.E.
Nov. 6, 1854	Noad, H. M., Ph.D., F.R.S., St. George's Hospital, S.W.
May 6, 1869	Noble, Captain A., Engineer, Elswick Ordnance Works, Newcastle
Jan. 15, 1863	Noble, John, Esq., Royal Arsenal General School, Woolwich, S.E.
April 4, 1861	Norrington, Frederick, Esq., 6, Roydon-villas, Clifton
Dec. 18, 1854	Norton, Fletcher, Esq., Broderick-street, Middleton, Cork

Date of Election.	
Jan. 17, 1848	Odling, William, M.B., F.R.S., Croydon, S., and Royal Institution, Albemarle-street, W.
Dec. 1, 1871	Ogg, Dr., Madras
May 4, 1871	Ogston, G. H., Esq., 22, Mincing-lane, E.C.
May 6, 1858	O'Neill, Charles, Esq., 17, North-bank, Regent's-park, N.W.
Nov. 4, 1869	Orme, Temple A., Esq., University College, W.C., and 46, Carlton-road, Kentish-town. N.W.
Feb. 7, 1867	Ottley, George, Esq., Carshalton, Surrey
Dec. 15, 1851	Oxland, Robert, Dr., Compton Gifford, near Plymouth
Nov. 15, 1866	Page, David, Esq., M.B., Kirkby Lonsdale, Westmoreland
April 7, 1870	Palmer, Alfred Neobard, 2, Risbygate-street, Bury St. Edmund's
Nov. 19, 1868	‖Palmer, Dr. W. J., care of Messrs. Grindlay, 55, Parliament-street, S.W.
Nov. 2, 1865	Parkinson, James, Esq., F.G.S., 25, Hereford-square, South Kensington, S.W.
Nov. 1, 1842	Parnell, Edward Andrew, Esq., Swansea
May 20, 1858	Parry, George, Esq., Ebbw Vale Iron, Steel, and Coal Company, Monmouthshire
April 21, 1870	Patchett, Isaac, F.R.A.S., Birstall, near Leeds
Mar. 17, 1870	Patterson, T. L., Esq., John Walker & Co., Greenock
Dec. 3, 1863	Pattinson, John, Esq., 75, Side, Newcastle-upon-Tyne
Mar. 5, 1868	‖Paul, Dr. B. H., Analytical Laboratory, 1, Victoria-street, Westminster, S.W.
Feb. 21, 1867	Payne, Martin Henry, Esq.,
Feb. 23, 1841	‖*Pearsall, Thomas, F.R.S.E., Mechanics' Institution, Southampton-buildings, Holborn, W.C.
Feb. 4, 1870	Pedler, Alexander, Esq., Wood Bank, Lordship-lane, Forest-hill, S.E.
Mar. 7, 1870	Penny, M. D., Misterton, near Gainsborough
Jan. 21, 1864	Pentecost, John, Esq., Beaumont, Wordsley, Stourbridge
April 4, 1843	Pepper, John Henry, Esq., 61, Boundary-road, St. John's-wood, N.W.
Feb. 2, 1865	Percival, Richard, Esq., The Shrubbery, Bexley Heath, Kent
Dec. 15, 1856	‖Perkin, W. H., F.R.S., Seymour Villa, Sudbury, Middlesex
Mar. 6, 1862	‖Perrins, J. D., Esq., Davenham Bank, Malvern
May 2, 1867	Peterson, F. W., Esq., H.M. Mint, Calcutta
Mar. 15, 1866	‖Phillips, C. P., Esq., 109, Fenchurch-street, E.C.
Jan. 18, 1842	Phillips, J. Arthur, Esq., Cressington-park, Aigburth, Liverpool
Jan. 16, 1862	Phipson, T. L., Ph.D., 4, The Cedars, Putney
Mar. 16, 1871	Piesse, C. H., Esq., 1, Merton-place, Chiswick, W.
Dec. 4, 1862	Piesse, G. W. S., Esq., Ph.D., 2, New Bond-street, W.
Nov. 15, 1860	‖Player, J. H., Esq., 111, Hagley-road, Edgbaston, near Birmingham
Feb. 23, 1841	‖*Playfair, Lyon, Ph.D., C.B., F.R.S., 4, Queensbury-place, South Kensington
Jan. 19, 1860	Plunket, Wm, Esq., Royal College of Science, Stephen's-green, Dublin
April 1, 1858	Pochin, Henry Davis, Esq., Barn Elms, Barnes, Surrey
Mar. 21, 1853	Pollock, Henry, Esq., 18, Hanover-terrace, Regent's-park, N.W.
Dec. 4, 1848	Pontifex, Edmund A., Esq., A.T.C.E., 1, Cleveland-gdns., Hyde-park, W.
June 16, 1864	Pontifex, S. R., Esq., George Town, Demerara.
Mar. 6, 1862	Pooley, T. A., Esq., Southside, Clapham Common, S.W.
Jan. 19, 1871	Potts, Edward, 163, High-street, Sunderland
Feb. 17, 1870	Prangley, Arthur, Esq., Laurel-bank, Clevedon, Somerset
May 19, 1864	‖Prentice, Manning, Esq., 2, Surbiton-villas, Violet-hill, Stowmarket.
May 16, 1861	Prestwich, Joseph, Esq., F.R.S., Shoreham, near Sevenoaks
Mar. 3, 1851	Price, Astley Paston, Ph.D., 47, Lincoln's-inn-fields, W.C.
June 3, 1850	Price, David Simpson, Ph.D., 26, Great George-street, Westminster
Feb. 17, 1870	Pritchard, William, Esq., Royal Veterinary College, N.W.
May 3, 1860	Procter, William, M.D., 24, Peter-gate, York
June 15, 1871	Proctor, Henry R., Esq., Clementhorpe, North Shields
Feb. 1, 1866	Purser, Edward, jun., Esq., 116, Fenchurch-street, E.C.

Date of Election.	
April 18, 1843	Randall, William B., Esq., Basset, Southampton
Jan. 16, 1862	Rayner, H., Esq., Smethwick, near Birmingham
Nov. 7, 1843	Redwood, Theophilus, Ph.D., Pharmaceutical Society, Bloomsbury-square, W.C., and Earlscroft, Lower Clapton-road, N.E.
Jan. 18, 1866	Redwood, T. B., Esq., Earlscroft, Lower Clapton-road, N.E.
Feb. 2, 1865	Reid, John, Esq., The Place, Monswald, Dumfriesshire
May 6, 1869	Reinold, A. W., Esq., Christchurch, Oxford
	Reynolds, Colonel, J. W., Army and Navy Club, St. James'-square, S.W.
Nov. 19, 1857	Reynolds, Richard, Esq., 13, Briggate, Leeds
Feb. 16, 1871	Reynolds, W. J., Esq., 24, Mare-street, Hackney, N.E.
Dec. 4, 1862	Richards, James, Esq., Clifton-lodge, near Preston, Lancashire
April 19, 1866	Richardson, Joseph, jun., Esq., 16, Dawson-street, Manchester
Dec. 1, 1864	Richardson, J. G. F., Esq., Houghton House, Stoney-gate, Leicester
Feb. 3, 1845	‖Rickard, W. T., Esq., 6, Clyde-terrace, Grove-road, Mile-end, E.
June 18, 1868	Riddel, H. B., Esq., Whitefield House, Rothbury, Morpeth
Dec. 15, 1851	Riley, Edward, Esq., 31, Park-square, Leeds
Dec. 7, 1865	Ritchie, W. B., Esq., Mount Pottinger, Belfast
Mar. 3, 1864	Ritchie, William, jun., Esq., Kincaid-field House, Milton of Campsie, Glasgow
Nov. 7, 1866	Roberts, William Chandler, Esq., Royal Mint, E.
April 6, 1865	‖Robertson, George B., Esq., Inland Revenue, Somerset House, W.C.
May 3, 1866	Robinson, John, Esq., Clifton College, Bristol
Dec. 4, 1862	Rodwell, G. F., Esq., Marlborough College, Wiltshire
	Ronalds, Edmund, Ph.D., Bonnington House, Bonnington, Edinburgh
Dec. 17, 1855	Roscoe, H. E., Ph.D., F.R.S., Owen's College, Manchester
Feb. 17, 1870	Ross, Lewis Buttle, Esq., Driffield
Feb. 18, 1869	Rossiter, William, Esq., South London College, 91, Blackfriars-road, S.E., and White Hill House, Frimley
Nov. 2, 1865	Row, Frederic, Esq., High-street, Braintree
Dec. 17, 1868	Rowan, Thomas, Esq., North Woodside House, Glasgow
Mar. 21, 1848	Rowney, Thomas H., Ph.D., Queen's College, Galway
Mar. 20, 1862	Royle, Thomas, Esq., Crayford, S.E.
Jan. 21, 1858	Rumney Robert, Esq., Ardwick Chemical Works, Manchester
Mar. 3, 1851	‖Russell, W. J., Ph.D., 34, Upper Hamilton-ter., St. John's-wood, N.W., and St. Bartholomew's Hospital, E.C.
	‖Rylands, Thomas Glazebrook, Esq., F.L.S., Heath-house, Warrington
June 18, 1868	Sadler, S. A., Dr. F.C.S., 69, Marton-road, Middlesbrough
April 16, 1863	‖Salt, Henry, Esq., M.B.C.M., F.R.G.S., 29, Gordon-square, W.C.
Feb. 17, 1859	‖Salter, Thomas, W., Esq., St. John's-cottage, Battersea-rise
June 25, 1871	‖Salter, Mortyn John, Esq., 26, Horton-road, Dalston
Nov. 6, 1854	Samuelson, Newton, Esq., F.C.S., Middlesbro'-on-Tees
March 3, 1870	Sandberg, C. P., Esq., 19, Great George-street, Westminster
Feb. 6, 1868	Schenk, Dr., 44, Dalyell-road, Stockwell-park, S.W.
Mar. 15, 1842	Schunck, Edward, Ph.D., F.R.S., Oaklands, Kersall, Manchester
May 17, 1842	Schweitzer, Edward G., Esq., 26, Westbourne-park, W.
May 4, 1870	Schweitzer, J., 86, King's-road, Brighton
June 18, 1863	Scorgie, James, Esq., Free General Assembly's Institution, Bombay
Dec. 1, 1864	Scott, Colonel H. Y. D., R.E., Ealing, W.
Jan. 20, 1870	Seward, Henry, 15, Barnsbury-park, London, N.
Dec. 15, 1859	Sibson, Alfred, Esq., 11, Eaton-terrace, St. John's-wood, N.W.
Nov. 3, 1870	Siemens, C. W., F.R.S., 3, Gt. George, Westminster
	Simpson, Maxwell, M.B., F.R.S., 17, Sutherland-place, Westbourne-park, Bayswater, W.
Mar. 15, 1852	Smee, Alfred, F.R.S., 7, Finsbury-circus, E.C.
Feb. 5, 1863	Smee, A. Hutchinson, jun., Esq., 7, Finsbury-circus, E.C.
Feb. 2, 1865	Smith, Arthur, Esq., Pera Lodge, Loughborough-road, Brixton, S.
Feb. 23, 1841	*Smith, J. Denham, Esq., Kenton-lodge, Middlesex, N.W.

Date of Election.	
April 7, 1856	Smith, Thomas J., F.G.S., Hessle, near Hull, and 10, North Church-side, Hull
Jan. 16, 1854	Smith, H. J., B.A., F.R.S., Balliol College, Oxford
Feb. 3, 1845	Smith, Robert Angus, Ph.D., F.R.S., 20, Devonshire-street, Manchester
Dec. 6, 1852	‖Smith, John, M.D., Sydney
Jan. 18, 1866	Smith, R. H., Esq., Bower-bank, Adelaide-place, Glossop-road, Sheffield
Dec. 20, 1866	Smith, Watson, jun., Esq., Hawthorn House, Wilmslow, Cheshire
Dec. 19, 1867	Smith, Dr. Frank, 79, Norfolk-street, Sheffield
Dec. 9, 1869	Smith, Edward, Esq., The Strand, Torquay
Feb. 16, 1871	Smith, William, 11, Allanton-terrace, Crosshill, Glasgow
March 17, 1870	Smith, S. T., E.C., F.G.S., 1, Park-prospect, Great Queen-street, Westminster, S.W.
June 21, 1866	Sparks, E. I., Esq., Crewkerne, Somerset
Jan. 18, 1866	Speir, James, Esq., Messrs. Barclay and Speir, Newcastle-on-Tyne
Dec. 1, 1864	Spence, J. B., Esq., Newton-heath, near Manchester
May 1, 1862	Spence, Peter, Esq., Pendleton Alum Works, Newton-heath, Manchester
April 7, 1851	Spencer, Thomas, Esq., 32, Euston-square, N.W.
Feb. 3, 1859	Spiller, John, Esq., 35, Grosvenor-road, Highbury New Park, N.
Jan. 15, 1863	‖Spiller, William, Esq., Atlas Dye Works, Hackney-wick, N.E.
Dec. 1, 1864	Sprengel, Hermann, Ph.D., 79, Gloucester-street, Pimlico, S.W.
Feb. 4, 1858	Squire, W. Stevens, Ph.D., 37, Acacia-road, Regent's-park, N.W.
April 21, 1859	‖Stanford, Edward Charles, Esq., Edinbarnet, by Dantocher, Dumbartonshire
Mar. 17, 1864	Staples, B. C., Esq., Sydenham-road North, Croydon, S.
April 19, 1860	Stark, M. J., Esq., Norwich
Dec. 15 1870	Stark, James F., Staffordshire Works, Oldbury, near Birmingham
May 5, 1870	Steel, James, F.R.S.S.A., 103, St. Vincent-street, Glasgow
Feb. 23, 1841	*Stenhouse, John, LL.D., F.R.S., 17, Rodney-street, Pentonville, N.
April 5, 1866	Stevens, William Carr, Esq., 33, Mark-lane, E.C.
Dec. 20, 1847	Stevenson, James C., Esq., Jarrow Chemical Works, South Shields
Feb. 18, 1864	Stevenson, Thomas, M.D., Guy's Hospital, S.E.; and 21, Caversham-road, N.W.
Dec. 15, 1864	Stewart, A. Y., Esq., Apothecaries'-hall, Blackfriars, E.C.
Mar. 7, 1867	Stewart, Major, R. C., Deputy Assistant Adj.-General, Horse Guards, and 12, Prince of Wales's-terrace, Kensington-palace, W.
June 21, 1866	Stock, W. F. K., Esq., F.C.S., Eppleby House, Eppleby-by-Darlington
Dec. 17, 1868	Stoddart, W. Walter, Esq., Laboratory, 9, North-street, Bristol
May 19, 1851	Stone, Daniel, Esq., Royal School of Medicine, Faulkner-st., Manchester
Jan. 16, 1862	Storey, J., Esq., Messrs. Storey, Bros., and Co., Heron Chemical Works, Lancaster
April 20, 1871	Sutcliffe, George, 34, East View, Preston
April 19, 1860	Sutton, F., Esq., Laboratory, Bank Plain, Norwich
June 15, 1865	‖Sweeting, G. B., Esq., King's Lynn, Norfolk
April 3, 1862	Symons, William, Esq., 26, Joy-street, Barnstaple, Devon
Dec. 5, 1867	Tatlock, Robert R., Esq., Assay Office, George-street, Glasgow
Nov. 6, 1854	Taylor, Jas., Esq., Farmers' Club, Salisbury-square, Fleet-street, E.C.
Mar. 16, 1846	Taylor, Thomas, Esq., Lecturer on Chemistry, Middlesex Hospital, Warwick House, Warwick-place, Grove End-road, N.W.
June 1, 1841	Tennant, James, Esq., 149, Strand, W.C.
May 5, 1864	Teschemacher, E. F., Esq., 1, Highbury-park North
April 15, 1858	‖Thomas, T., Esq., Begbrook, Frenchay, Bristol
Nov. 17, 1859	‖Thomas, Andrew, Esq., 13, Hendley-street, Adelaide, South Australia
Jan. 16, 1862	Thomas, R. W., Esq., 10, Pall Mall, S.W.
Feb. 5, 1863	Thompson, R. E., M.D., 21, South-street, Park-lane, W.
Dec. 20, 1866	Thomson, Prof. A. M., University, Sydney, N.S.W.
April 15, 1858	‖Thomson, John, Esq., 7, Lower Kennington-lane, S.
Mar. 4, 1858	Thornthwaite, William, Esq., 123, Newgate-street, E.C.

Date of Election.	
Feb. 1, 1866	‖Thorp, William, jun., Esq., 39, Sandringham-road, West Hackney, N.E.
Feb. 16, 1871	Thorpe, T. E., Ph.D., F.R.S.E., Andersonian University, Glasgow, and 46, Windsor-terrace, Glasgow
Dec. 20, 1860	Thudicum, John L. W., M.D., 3, Pembroke-road, Kensington, W.
Feb. 19, 1863	Tichborne, C. R. C., Esq., M.R.I.A., Apothecaries' Hall of Ireland, Dublin
Dec. 5, 1867	Tidy, C. M., Esq., M.B., The Hollies, Cambridge-heath, Hackney, N.E.
June 1, 1865	Tilden, William A., Esq., D.Sc, 17, Bloomsbury-square, W.C.
June 20, 1853	‖Tomlin, Andrew, Esq., Valparaiso
June 2, 1864	Tomlinson, Charles, Esq., F.R.S., 3, Ridgmount, Highgate, N.
Jan. 15, 1855	‖Tookey, Charles, Esq., Museum of Practical Geology, Jermyn-street, S.W.
Dec. 3, 1868	Tosh, Dr. E. G., Laboratory, Whitehaven
Mar. 21, 1867	Tribe, Alfred, Esq., 73, Artesian-road, Bayswater, W.
Nov. 3, 1856	Tuson, Richard V., Esq., Royal Veterinary College, N.W.
Feb. 2, 1871	Tustin, John Robert, Hatcham Manor Works, Manor-street, Old Kent-road, and 9, Paragon, Blackheath
June 2, 1870	Tustin, W.B., Hatcham Manor Works, Manor-street, Old Kent-road, and 9, Parogan, Blackheath
April 2, 1868	‖Tyndall, Dr. John, F.R.S., Royal Institution, Albemarle-street, W.
Nov. 16, 1865	Umney, Charles, Esq., 40, Aldersgate-street, E.C.
May 18, 1865	Upward, Alfred, Esq., Chartered Gas Works, 146, Goswell-street, E.C.
Feb. 2, 1865	‖Vacher, Arthur, Esq., 20, Great Marlborough-street, W.
June 3, 1869	Valentin, W., Esq., 126, Lancaster-road, Notting Hill, W.
Nov. 7, 1866	Vaughan, E. P. H., Esq., 54, Chancery-lane, W.C.
Dec. 17, 1849	Voelcker, A., Ph.D., F.R.S., 39, Argyle-road, Kensington, W.
April 17, 1862	Von Bose, C. Moritz, Esq., Messrs. Gehe and Co., Chemical Works, Dresden
April 5, 1866	Vosper, Thomas, Esq., 27, Nightingale-street, Strangeways, Manchester
Feb. 21, 1867	Waite, William Thurston, Esq.
Dec. 18, 1843	Waldie, David, Esq., Calcutta
Feb. 15, 1866	Walenn, W. H., Esq., 74, Brecknock-road, N.
Feb. 2, 1865	‖Walker, J. F., Esq., 16, Gilly-gate, York, and Sidney College, Cambridge
Jan. 16, 1868	‖Walker, Captain Alexander, R.A., Commissary of Ordnance, Allahabad, India
Dec. 15, 1856	Wallace, William, Esq., Ph.D., F.R.S.E., Chemical Laboratory, 42, Bath-street, Glasgow
Dec. 9, 1869	Walton, Thomas, Esq., 3, Bourne-street, Hull
April 21, 1864	Ward, George, Esq., Laboratory, Mechanics' Institution and Literary Society, Leeds
Dec. 21, 1865	Ward, Thomas, Esq., Arnold Villas, South Shore, Blackpool
Jan. 6, 1845	Ward, William Sykes, Esq., Denison-hall, Leeds
April 20, 1871	Ward, William, Sheffield Moor, Sheffield
Mar. 19, 1863	‖Warington, George, Esq., 1, Conduit-vale, Greenwich, S.E.
Mar. 19, 1863	‖Warington, Robert, Esq., Atlas Chemical Works, Millwall, E.; and 1, Conduit-vale, Greenwich
Dec. 3, 1857	‖Watson, Henry Hough, Esq., The Folds, Bolton-le-Moors
Feb. 4, 1858	Watson, J. Forbes, M.A., M.D., India Museum, India Office, S.W.
Dec. 20, 1847	Watts, Henry, Esq., B.A., F.R.S., 151, King Henry's-road, N.W.
April 19, 1866	Watts, W. M., Esq., Beechfield, Bowdon, near Manchester
April 20, 1846	Way, John Thomas, Esq., 9, Russell-road, Kensington, W.
Mar. 1, 1866	Webster, W., Esq., F.C.S., 9, Bridge-street-row, Chester
Feb. 21, 1861	Weston, William, Esq., Chemical Department, Portsmouth Dockyard
June 2, 1851	‖Whipple, George, Esq., 10, Mortimer-road, De Beauvoir-square, Kingsland, N.
	White, Alfred, F.L.S., West Drayton
Mar. 20, 1862	White, Leedham, Esq., 17, Millbank-street, Westminster, S.W.

Date of Election.	
Mar. 5, 1868	White, T. W., Esq., Ifield, near Crawley, Sussex
Nov. 5, 1863	Whitfield, John, Esq., 113, Westborough, Scarborough
Dec. 9, 1869	Wiggin, John, Esq., 34, St. Matthew's, Ipswich
June 17, 1858	Williams, John, Esq., 5, New Cavendish-street, W.
May 18, 1857	Williams, W. Mattieu, Esq., Woodside-green, Croydon
Jan. 16, 1862	‖Williams, C. Greville, Esq., F.R.S., 4, Oxford-road, Turnham Green, W.
Jan. 21, 1869	Williams, Rev. Stephen, Stonyhurst College, Blackburn
May 15, 1848	‖Williamson, A. W., Ph.D., F.R.S., University College, W.C.
June 15, 1871	Willmore, Charles, Queenwood College, near Stockbridge, Hants
Feb. 17, 1870	Wills, Thomas, Royal Institution, Albemarle-street, W.
June 7, 1866	Wilson, C. C., Esq., Bridgwater Smelting Company, St. Helens, Lancashire
Nov. 19, 1855	Wilson, G. F., Esq., F.R.S., Heatherbank, Weybridge-heath
Dec. 4, 1862	Wilson, J. C., Esq., School of Medicine, Leeds
May 3, 1852	Wilson, William, Esq., Jubilee-street, Mile-end, E.
Mar. 2, 1857	Winstone, Benjamin, M.D., 7, Ely-place, E.C.
May 7, 1863	Wood, Thomas, Ph.D., 23, Grove-street, Alpha-road, N.W.
Dec. 5, 1867	Wood, Augustus A., Esq., 74, Cheapside, E.C.
Jan. 19, 1860	‖Wood, Charles Henry, Esq., 25, Devonshire-road, Seven Sisters'-road, N.
Feb. 4, 1858	‖Worsley, Philip, J., Esq., 1, Codrington-place, Clifton, Bristol
June 7, 1866	Wright, Charles R. A., D.Sc., St. Mary's Hospital, Paddington, W.
Feb. 17, 1870	Wright, Philip, The Elms, Ripley, Derbyshire
May 16, 1861	Wright, W. C., Esq., 46, Mosley-street, Manchester
Feb. 4, 1864	Wrightson, John, Esq., Royal Agricultural College, Cirencester
May 19, 1864	Wrightson, Francis, Ph.D., Nine Elms, King's Norton, near Birmingham
Feb. 2, 1865	Wyndham, Heathcote, Esq., Merton College, Oxford
Feb. 23, 1841	*Yorke, Colonel Philip, F.R.S., 89, Eaton-place, Belgrave-square, S.W.
	Young, James, Esq., Kelly, Wering's Bay by Greenock, N.B.

ASSOCIATES.

	Richter, Reinhold, Esq., Harpenden near St. Albans
Nov. 4, 1869	Gerstl, R., Esq., University College, W.C.

FOREIGN MEMBERS.

NUMBER NOT TO EXCEED FORTY.

Date of Election.	
Jan. 20, 1851	Balard, A. J., Collége de France, Paris
Mar. 1, 1860	Berthelot, M., Collége de France, Paris
June 18, 1849	Boussingault, J. B., Paris
Feb. 1, 1842	Bunsen, R. W., Ph. D., F.R.S., University of Heidelberg
May 18, 1858	Cahours, Auguste, à la Monnaie, Paris
June 19, 1862	Canizzaro, S., University of Palermo
June 18, 1849	Chevreul, Michel Eugène, F.R.S., Jardin des Plantes, Paris
April 21, 1864	Dessaignes, Victor, M.D., Vendôme, Dep. Loire-et-Cher, France
Mar. 1, 1860	Deville, Henri Sainte Claire, Ecole Normale, Paris
Dec. 6, 1847	Dumas, Jean Baptiste, F.R.S., Paris
April 21, 1864	Fehling, Hermann von, Ph. D., Stuttgart
Mar. 1, 1860	Fremy, Edmond, Ecole Polytechnique, Paris
Nov. 4, 1844	Fresenius, C. Remigius, Ph. D., Wiesbaden
Mar. 1, 1860	Fritzsche, J., St. Petersburgh
May 3, 1866	Gibbs, Professor Wolcott, Cambridge, Massachussets, U.S.
June 19, 1862	Kekulé, A., Ph. D., University of Bonn
May 17, 1847	Kolbe, Hermann, Ph. D., University of Leipzig
June 18, 1849	Kopp, Hermann, Ph. D., University of Heidelberg
June 1, 1841	Liebig, Baron Justus von, F.R.S., University of Munich
June 19, 1862	Loewig, C., Ph. D., University of Breslau
June 19, 1862	Malaguti, Rennes, Brittany
June 19, 1862	Marignac, Jean Charles, Geneva
Mar. 1, 1860	Mulder, G. J., Bennekom, près de Wageningen, Pays-Bas
June 19, 1862	Pasteur, L., F.R.S., Ecole Normale, Paris
Mar. 1, 1860	Peligot, E., à la Monnaie, Paris
May 3, 1866	Rammelsberg, Professor, Berlin
June 18, 1849	Regnault, Henri Victor, F.R.S., Paris
	Schrötter, Ritter v. Cristelli, Director des Münzamts, Vienna
June 19, 1862	Stas, J. S., Ecole Militaire, Brussels
	Strecker, Adolph, Ph. D., University of Tübingen
April 18, 1843	Will, Heinrich, Ph. D., University of Giessen
June 18, 1849	Wöhler, F., F.R.S., University of Göttingen
	Wurtz, Adolphe, F.R.S., Ecole de Medicine, Paris
June 19, 1862	Zinin, Nicolaus, St. Petersburgh

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